

## Extrusion Processing of Green Biocomposites: Compounding, Fibrillation Efficiency, and Fiber Dispersion

Maiju Hietala,<sup>1,2</sup> Pierre Rollo,<sup>1</sup> Kaarina Kekäläinen,<sup>2</sup> Kristiina Oksman<sup>1\*</sup>

<sup>1</sup>Division of Materials Science, Department of Engineering Sciences and Mathematics, Luleå University of Technology, SE-97187 Luleå, Sweden

<sup>2</sup>Fibre and Particle Engineering Laboratory, Department of Process and Environmental Engineering, University of Oulu, FI-90014 Oulu, Finland

Correspondence to: K. Oksman (E-mail: kristiina.oksman@ltu.se)

**ABSTRACT:** The efficiency of twin-screw extrusion process to fibrillate cellulose fibers into micro/nanosize in the same step as the compounding of green bionanocomposites of thermoplastic starch (TPS) with 10 wt % fibers was examined. The effect of the processing setup on micro/nanofibrillation and fiber dispersion/distribution in starch was studied using two types of cellulose fibers: bleached wood fibers and TEMPO-oxidized cellulose fibers. A composite with cellulose nanofibers was prepared to examine the nanofiber distribution and dispersion in the starch and to compare the properties with the composites containing cellulose fibers. Optical microscopy, scanning electron microscopy, and UV/Vis spectroscopy showed that fibers were not nanofibrillated in the extrusion, but good dispersion and distribution of fibers in the starch matrix was obtained. The addition of cellulose fibers enhanced the mechanical properties of the TPS. Moisture uptake study revealed that the material containing TEMPO-oxidized fibers had higher moisture absorption than the other composites. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39981.

**KEYWORDS:** cellulose and other wood products; nanostructured polymers; biopolymers renewable polymers; microscopy; composites

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### INTRODUCTION

Renewability, biodegradability, abundance in nature, nontoxicity, high mechanical properties, high specific surface area; these are some of the features that give nanocellulose such great potential for use in a wide variety of applications ranging from green packaging to medical materials. Depending on the source and isolation method used, cellulose nanofibers (CNF) are typically 10–100 nm in diameter and several micrometers long<sup>1,2</sup> and, as opposed to the cellulose nanowhiskers prepared by the acid hydrolysis method, they contain both the amorphous and crystalline regions of cellulose.<sup>3</sup>

CNF are usually separated mechanically from lignocellulosic plants, such as wood and agricultural crops, after removal of lignin and other plant cell wall substances chemically.<sup>4,5</sup> The most typical methods currently used in the laboratory-scale preparation of CNF are high-pressure homogenization<sup>6–8</sup> and ultrafine grinding.<sup>9–11</sup> The isolation of nanofibers is considered as energy intensive process,<sup>12</sup> and in order to lower the cost and increase the commercial potential of CNF, more energy efficient ways to produce CNF are being studied. For example, to ease the mechanical separation of nanofibers, chemical,<sup>13–15</sup> or enzymatic<sup>16–18</sup> pretreatments of cellulose have been used. How-

ever, pretreatments add a cost to the nanofibers and they may also have negative effects on the cellulose properties. There are also studies showing that less-conventional methods, such as the twin-screw extrusion, can be used in defibration of wood fibers from wood particles,<sup>19–21</sup> or even as cost-efficient methods in isolation of cellulose micro or nanofibers from wood pulp.<sup>22–24</sup>

Thermoplastic starch (TPS)-based biodegradable biocomposites are a promising material to replace oil-based plastics in packaging and other short life-time applications,<sup>25,26</sup> and processing native starch granules together with a plasticizer into TPS under heat and shear is already a well-known method.<sup>25,27</sup> Earlier studies have also shown that preparation of TPS and compounding of cellulose nanocomposites can be done in one step using twin-screw extrusion.<sup>28–30</sup> The aim of this study was to combine the processing of starch into TPS as well as the composite compounding and nanofibrillation of cellulose in one extrusion step in order to manufacture green biocomposites of TPS and cellulose fibers. The advantage of this kind of processing would be more efficient and economical production of cellulose nanocomposites due to fewer processing steps. To study the effect of fiber treatment of the nanofibrillation, two different types of cellulose fibers were used as the cellulosic raw material; namely, bleached softwood fibers and TEMPO-oxidized



**Figure 1.** Used raw materials: (a) CNF, (b) TEMPO-oxidized fibers, and (c) BLWF.

hardwood fibers. The TEMPO-oxidized fibers were chosen to be used as the TEMPO-oxidation method has been shown to greatly reduce the mechanical energy needed for nanofibrillation.<sup>13,14</sup> In principle, in this method negatively charged carboxylate groups are introduced to the surface of cellulose microfibrils, creating repulsive forces between them and, thus, weakening the structure of the cellulose fiber.<sup>13,14</sup>

In this work, the ability to use twin-screw extrusion process to fibrillate cellulose fibers into micro or nanosize, and in the same process prepare green bionanocomposites of TPS with 10 wt % fiber content was studied. Microscopic methods [optical microscopy and scanning electron microscopy (SEM)] were used to examine the fiber size after extrusion and fiber distribution in the composites. As indirect measurements of the fiber size, dispersion and distribution, the properties of the prepared composites were analyzed by means of tensile testing, UV/Vis spectroscopy, and moisture uptake analysis and compared to those of a composite reinforced with 10 wt % of CNF.

## EXPERIMENTAL

### Materials

Softwood wood flour (Scandinavian Wood Fiber AB, Orsa, Sweden) with a particle size range of 200–400  $\mu\text{m}$  was used as a starting material for bleached wood fibers (BLWF) and CNF (Figure 1). Sodium chlorite (Sigma–Aldrich, Germany) and glacial acetic acid (Merck, Germany) were used in the delignification of wood flour. The average length and width of the BLWF was 0.54 mm and 27.5  $\mu\text{m}$ , respectively, determined using optical fiber analyzer Kajaani FiberLab (Metso Automation, Finland). Never-dried bleached hardwood kraft pulp (*Betula pendula*) with an average length and width of 0.88 mm and 20.7  $\mu\text{m}$  (Kajaani FiberLab) was used to prepare the TEMPO-oxidized cellulose fibers (Figure 1). 2,2,6,6-Tetramethylpiperidine-1-oxyl radical (TEMPO), sodium hypochlorite, sodium bromide, and sodium hydroxide used in the TEMPO-oxidation were purchased from Sigma–Aldrich.

CNF were obtained from delignified (bleached) softwood fibers through mechanical fibrillation, using an ultrafine grinder, a super masscolloider MKCA6-3 (Masuko Sangyo, Japan), at a rotational speed of 1440 rpm. The total grinding time was 16 min. A potato starch, ELIANE™ 100 (AVEBE, the Netherlands) with high amylopectin content (>99%) was used as matrix; D-sorbitol (Merck) was used as plasticizer for starch, and stearic acid (VWR, Leuven, Belgium) was used as a lubricant.

### Preparation of the BLWF

Following the same procedure used in our previous work,<sup>30</sup> the wood flour was delignified with acidified sodium chlorite solution using the Jayme–Wise method to obtain BLWF. Two hundred fifty grams of wood flour (dry mass) was treated in a flask containing 3500 mL deionized water with 5 mL acetic acid and 33.5 g of sodium chlorite at 70–75°C. Additions of acetic acid and sodium chlorite were continued at 2-h intervals until the wood became white, which in this case required 11 additions of acetic acid and sodium chlorite. The wood was washed twice during the treatment and at the end with a minimum of 60 L of deionized water. Before washing, the wood was left in the acidified chlorite solution for 12 h at 70–75°C. The total treatment time of the wood flour in acidified chlorite solution was 58 h.

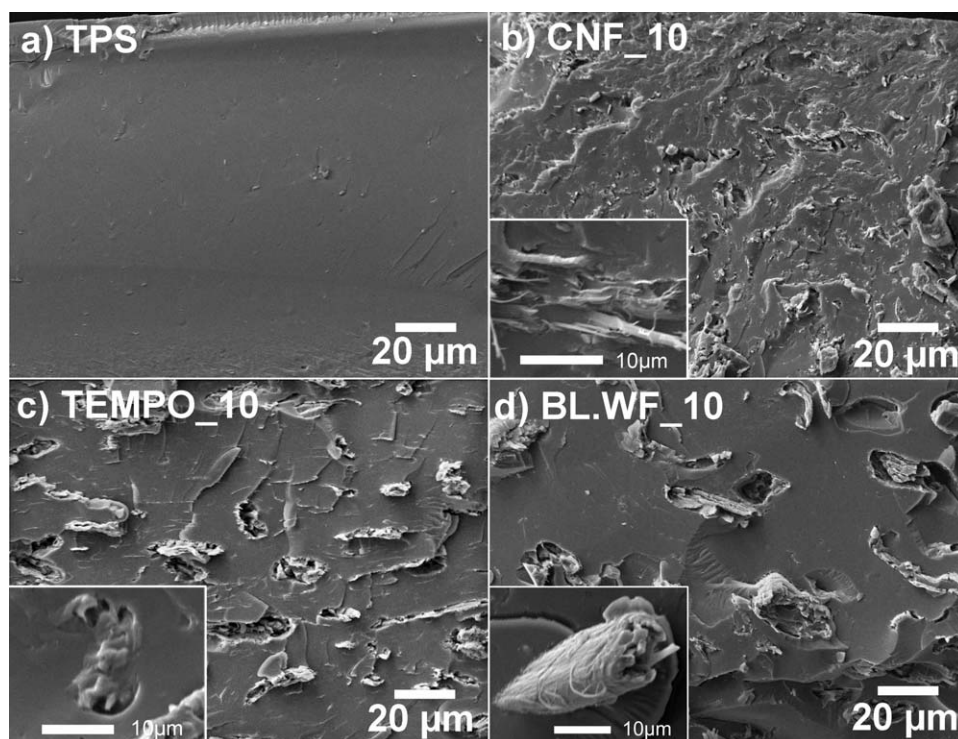
### Preparation of TEMPO-Oxidized Cellulose Fibers

The TEMPO-mediated oxidation was performed under alkaline conditions according to the procedure described by Saito et al.<sup>13,14</sup> Fifty grams of cellulose fibers was diluted to 1% consistency and 0.1 mmol/g of TEMPO, and 1 mmol/g of NaBr were added to the suspension. The reaction was started by adding 10% NaClO solution and the pH was adjusted to 10–10.5 and maintained at this level with 0.5M NaOH during the oxidation. Total amount of NaClO used was 10 mmol/g. The reaction was finished after 5.5 h and the oxidized fibers were washed with deionized water until the conductance of the filtrate reached a value under 10  $\mu\text{C}/\text{cm}$ . The carboxyl content of the oxidized sample was 1.3 mmol/g, and it was determined using conductometric titration in duplicate according to Araki et al.<sup>31</sup> and Katz and Beatson.<sup>32</sup>

### Composite Processing

The compounding of the neat TPS and the composites was done using twin-screw extrusion. Before extrusion, premixes of starch, sorbitol, stearic acid, and 10 wt % cellulose fibers were prepared using a Waring laboratory blender with short blending pulses of  $3 \times 3$ –5 s. Due to the low dry matter content of the TEMPO-oxidized fiber suspension (3.4 wt %), moisture content of the premix with TEMPO-oxidized fibers was 74 wt %; therefore, the water content of the other premixes was adjusted to the same level. The sorbitol content was 30 wt % and the content of stearic acid was 0.7 wt %, both based on the dry weight of starch. The stearic acid was added as a processing aid, preventing the compound from sticking to the screws or clogging the die.





**Figure 4.** Fracture surfaces of (a) neat TPS, (b) TPS reinforced with CNF, (c) TPS reinforced with TEMPO-oxidized fibers (TEMPO), and (d) TPS reinforced with BLWF.

10 days in a desiccator at 50% relative humidity (RH) in room temperature before testing. The specimens were kept in the desiccator until the moment they were going to be tested, to minimize the variations in the moisture content. The tensile properties of the materials were tested using an Instron 4411 tensile testing machine with a 500 N load cell, gauge length of 40 mm, and testing speed of 4 mM/min. At least six replicates of each material were tested. In addition to tensile modulus, tensile strength and elongation at break, the toughness of the materials was calculated as the area under the stress-strain curve.<sup>33</sup>

**Optical Properties.** The transparency of the neat TPS and the composite films was studied using a Perkin Elmer UV/Vis Spectrometer Lambda 2S (Überlingen, Germany). The light transmittance of the films was measured in a light wavelength area from 300 to 1000 nm at a scanning speed of 240 nm/min. Three replicates of each material were measured.

**Moisture Uptake.** The moisture uptake of the prepared materials was studied by exposing the samples to 97–98% RH using a desiccator containing a saturated salt solution of potassium sulfate,  $K_2SO_4$ . The desiccator was kept in room temperature. Specimens were cut from the compression-molded films, and the specimen size was  $40 \times 40 \times 0.4 \text{ mm}^3$ . Minimum of three replicates of each material were used in the analysis. First, the specimens were dried overnight in an oven at  $65^\circ\text{C}$  and then weighed. The average weight of the dried specimen was 0.7 g. The oven-dry samples were placed in a desiccator with 98% RH in room temperature, and after specific time (17 and 30 days) the specimens were removed from the desiccator and weighed.

The moisture uptake was determined as the gain of weight during this time. Due the degradation of the films, especially of the neat TPS film, it was difficult to continue the experiment longer than 1 month.

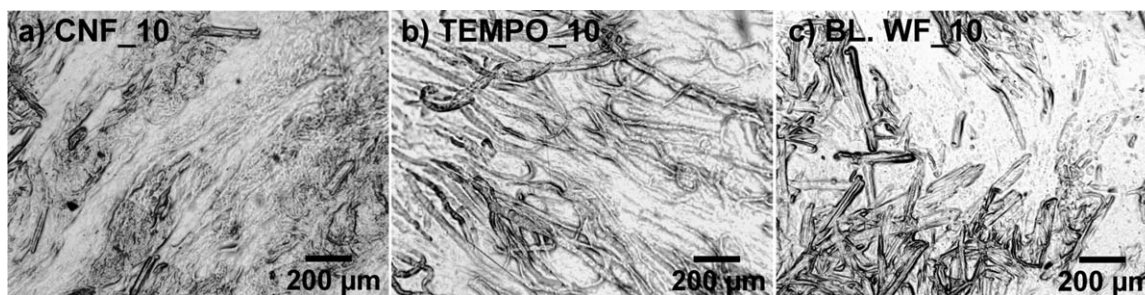
**Statistical Analysis.** One-way analysis of variance (ANOVA) followed by Tukey–Kramer multiple comparison tests with a 0.05 significance level was used to analyze the results from mechanical testing and from the moisture uptake study.

## RESULTS AND DISCUSSION

### Microscopy of the Composites

In the SEM study of fractured surfaces of the TPS and the composite with 10% of CNF are compared with composites with TEMPO-oxidized fibers and BLWF. The SEM images of the fractured surfaces are shown in Figure 4. From Figure 4, it is possible to see that the nanofibers are rather well dispersed and distributed in the TPS matrix [Figure 4(b)], as well as that the fiber size is increasing in [Figure 4(c)] TEMPO-oxidized fibers and [Figure 4(d)] BLWF. These fibers are several micrometers in size, indicating that the shear forces in twin-screw extrusion have not been enough to fibrillate fibers into nanosize. When comparing the fracture surfaces of the composites with BLWF [Figure 4(d)] and TEMPO-oxidized fibers [Figure 4(c)], the TEMPO-oxidized fibers appear to be smaller. However, the reason for this is most likely the smaller size of the original fibers due to the different fiber source (birch).

The smaller images inserted in Figure 4 provide more details from the fracture surfaces of the composites. In the case of TPS reinforced with CNF, some aggregated nanofibers or



**Figure 5.** Optical microscopy images of the TPS films reinforced with 10 wt % of cellulose fibers: (a) CNF, (b) TEMPO-oxidized fibers, and (c) BLWF.

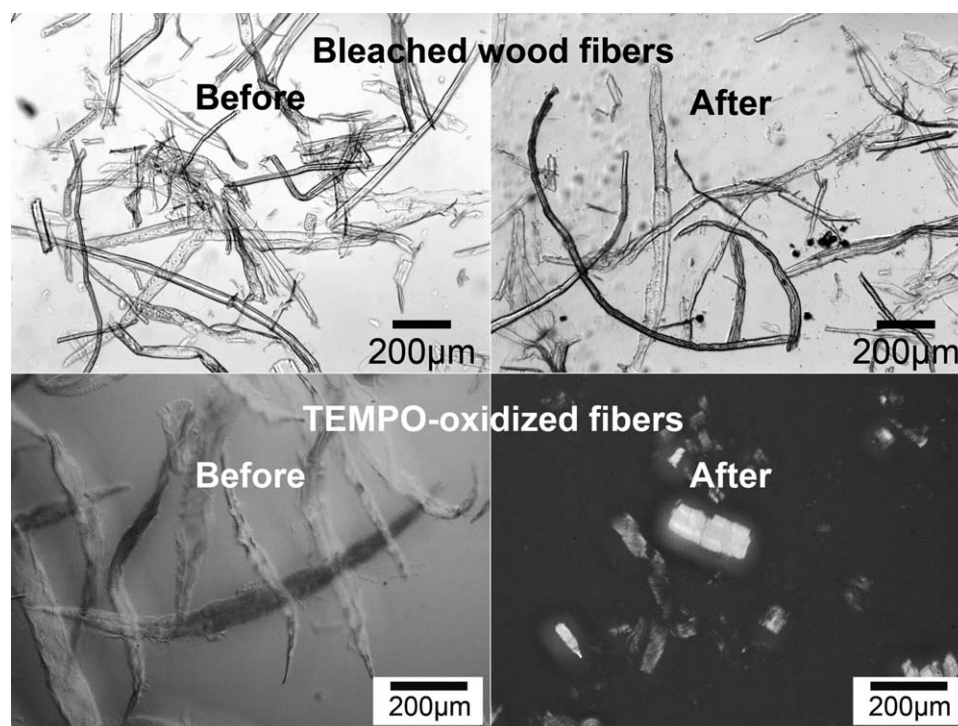
nonfibrillated fibers could be seen in the fracture surface [down left corner in Figure 4(b)], even though the overall distribution of nanofibers was rather good [Figure 4(b)]. Some gaps existed between the fibers and the TPS matrix in the composite reinforced with TEMPO-oxidized fibers [down left corner in Figure 4(c)], perhaps due to the swelling of fibers as a result of the TEMPO-oxidation treatment, which could impair the mechanical properties of this material.

Because the TPS matrix has high transparency, optical microscopy was used to obtain more information of the distribution and dispersion of the fibers in the starch films (Figure 5). The distribution of fibers was rather good in all the composites, though in the material made with 10% BLWF some less homogeneous areas could be seen [Figure 5(c)]. The observation made from the SEM images can be confirmed from the optical microscopy images: the BLWF and TEMPO-oxidized fibers have not been fibrillated into nanofibers and, also in the film of TPS reinforced with CNF, some nonfibrillated fibers can be seen.

#### Fiber Characteristics After Extrusion

After extrusion, the TPS matrix was removed from the composites for fiber size estimation. Figure 6 shows the optical microscopy images of the BLWF and TEMPO-oxidized fibers before and after twin-screw extrusion. As Figure 6 shows, the fiber length and diameter do not seem to be affected much in the case of BLWF. The TEMPO-oxidized fibers, conversely, appear to be shortened when compared to the fibers before extrusion, indicating that the aspect ratio of the TEMPO-oxidized fibers is lower than that of BLWF.

As filtration was used to separate the fibers from the dissolved matrix, there is also a possibility that some of the smaller fibrils are lost if they are small enough to pass the filter paper. However, Figure 6 still provides a good understanding of the effect of extrusion on the fiber size regarding the larger fibers. To obtain a better comprehension of the size of the fibers after processing, the fiber sizes were also measured using optical fiber analyzer, and the results from the analysis are shown in Table I.



**Figure 6.** BLWF and TEMPO-oxidized fibers before compounding with starch and after compounding and removal of the TPS matrix. The images from TEMPO-oxidized fibers were taken using a polarizing filter.

**Table I.** The Average Lengths and Widths of the TEMPO-Oxidized Fibers and BLWF Before and After Compounding Measured Using Kajaani Fiberlab

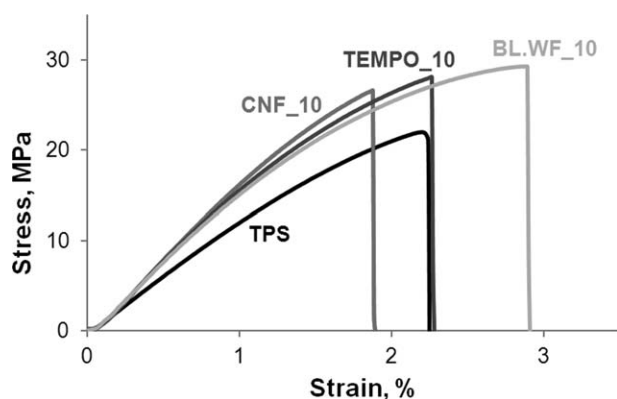
Fiber type	Width ( $\mu\text{m}$ )	Length, L(l) (mm)	Fines (%)	Number of measured fibers
BLWF before	27.46	0.54	21.99	13,041
BLWF after	27.22	0.47	24.43	13,573
TEMPO before	22.45	0.56	26.84	14,451
TEMPO after	19.54	0.14	83.95	6968

The resolution of the camera used to measure fiber lengths in the FiberLab analyzer is 10  $\mu\text{m}$ , so the possible nanosize fibrils cannot be measured using this technique, but the results from the fiber analysis support the conclusions made from Figure 6. The BLWF are not affected much by the extrusion process, however, the average length of TEMPO-oxidized fibers is reduced to 0.14 mm and also the fines content (particles shorter than 200  $\mu\text{m}$ ) of the TEMPO-oxidized sample after extrusion is larger compared to the other samples (Table I).

A possible explanation for not obtaining nanofibers using these extrusion conditions can be the high water content of the used premixes (74%) resulting in low viscosity of the starch-fiber melt inside the extruder, as the shear stress in a twin-screw extruder is affected by the viscosity of the melt, shear rate, shear stress, and the duration of the stress (i.e., the residence time under load).<sup>34</sup> The use of other type of extruder, such as counter-rotating twin-screw extruder, to increase the shear, might result in better nanofibrillation of cellulose fibers, as in the case of nanoclay reinforced polymer composites better exfoliation and dispersion of clay platelets have been obtained when using counter-rotating twin-screw extruder in comparison with corotating twin-screw extruder.<sup>35,36</sup>

### Mechanical Properties of the Materials

Typical stress-strain curves of the films of neat TPS and TPS reinforced with 10% of CNF, TEMPO-oxidized fibers (TEMPO), and BLWF are shown in Figure 7, and the results obtained from the tensile testing are summarized in Table II.

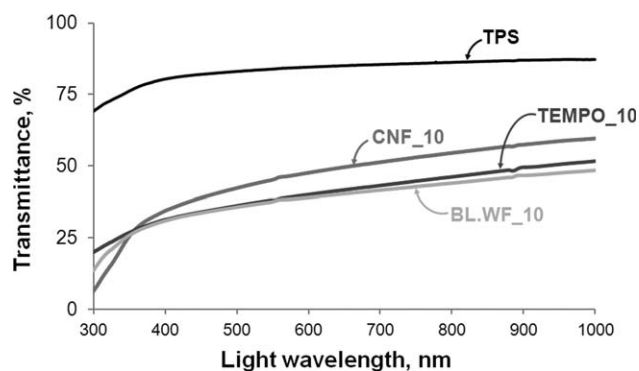
**Figure 7.** Typical stress-strain curves of the prepared materials.**Table II.** Mechanical Properties of the Films of TPS and TPS Reinforced with 10 wt % of CNF, TEMPO-Oxidized Fibers (TEMPO), and BLWF Together with Standard Deviations

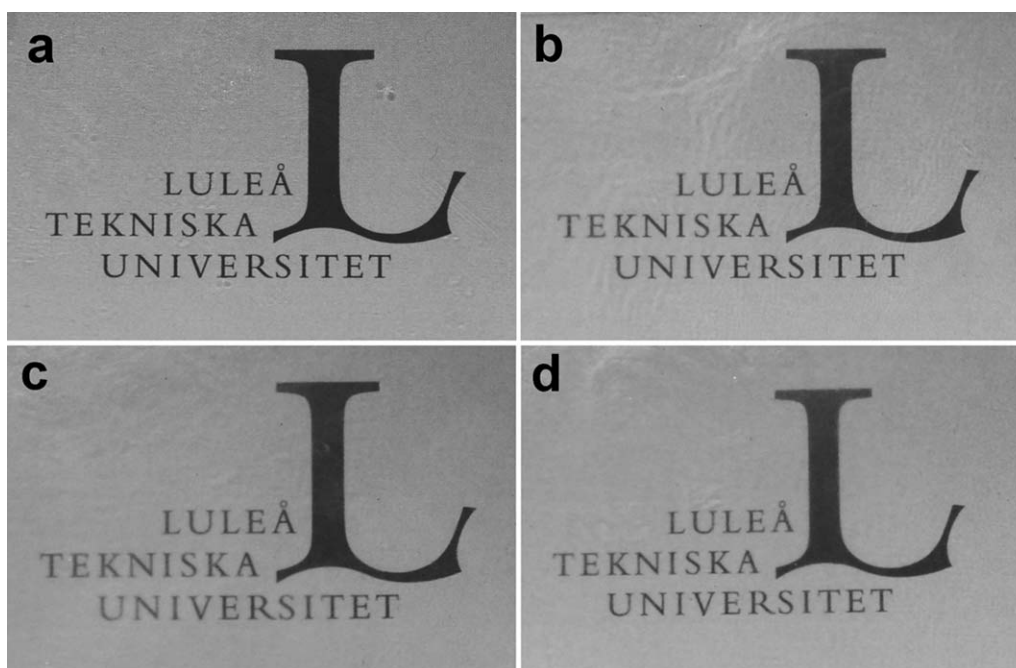
Material	Tensile strength <sup>a</sup> (MPa)	Young's modulus <sup>a</sup> (GPa)	Elongation at break <sup>a</sup> (%)
TPS	24.2 $\pm$ 1.3 <sup>a</sup>	1.36 $\pm$ 0.06 <sup>a</sup>	2.6 $\pm$ 0.3 <sup>a</sup>
CNF_10	27.2 $\pm$ 2.0 <sup>b</sup>	1.83 $\pm$ 0.11 <sup>b</sup>	2.2 $\pm$ 0.4 <sup>a</sup>
TEMPO_10	28.1 $\pm$ 1.5 <sup>b</sup>	1.72 $\pm$ 0.06 <sup>c</sup>	2.4 $\pm$ 0.3 <sup>a</sup>
BLWF_10	27.9 $\pm$ 1.9 <sup>b</sup>	1.79 $\pm$ 0.05 <sup>b,c</sup>	2.6 $\pm$ 0.4 <sup>a</sup>

<sup>a</sup> Means marked with the same superscript letter within the same column are not significantly different at 5% significance level based on the ANOVA and Tukey-Kramer pairwise comparison test.

From Figure 7 and Table II, it can be seen that the addition of cellulose increased the stiffness and the strength of the TPS. In the Figure 7, it is also possible to see that the composites with BLWF and TEMPO-oxidized fibers have better toughness compared to the TPS. The tensile modulus was increased by 27–34% and the strength by 12–16% from the neat TPS. Greater improvements in modulus and strength have been reported earlier for TPS reinforced with 10 wt % of CNF in relation to neat TPS,<sup>37–39</sup> however, in these cases, the properties of the neat matrix have been much lower than in the present study. For example, López-Rubio et al.<sup>38</sup> reported modulus of 24 MPa, strength of 1.8 MPa for amylopectin starch films with 38 wt % of glycerol prepared using solution casting method, whereas the TPS matrix prepared here had elastic modulus of 1.36 GPa and strength of 24 MPa. The stiffness and strength of the neat TPS were also higher compared to our earlier results in which the same raw materials were used.<sup>30</sup> Reason for this can be the recrystallization of amylopectin which has been shown to be affected by factors such as the moisture content, storage conditions, and storage time of TPS.<sup>40</sup>

Quite unexpectedly, there were no significant differences in the mechanical properties of the composites with different types of cellulose fiber (BLWF, TEMPO-oxidized fibers, or CNF). In general, composites with CNF are presumed to result in better

**Figure 8.** The light transmittance of neat TPS and TPS/cellulose fiber composites with 10 wt % of CNF, TEMPO-oxidized fibers (TEMPO), and BLWF.



**Figure 9.** Visual appearance of the films: (a) TPS, (b) TPS with 10 wt % of CNF, (c) TPS with 10 wt % TEMPO-oxidized fibers, and (d) TPS with 10 wt % BLWF.

mechanical performance than composites reinforced with macro-sized cellulose fibers.<sup>3,41</sup> For this reason, it is thought that the dispersion of CNF needs to be improved further, even though it was better in comparison with our earlier study in which cellulose nanocomposites were prepared by extrusion.<sup>30</sup>

### Optical Properties

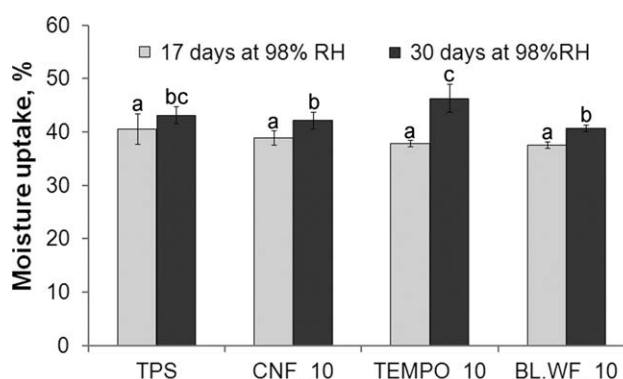
Transparency can be used as an indirect measure of the size and dispersion of cellulose fibers in the matrix, since, if the reinforcement is not in nanoscale (nonfibrillated cellulose fibers, aggregated nanofibers), the light transmittance of the material decreases due to the increased light scattering.<sup>2,42</sup> Figure 8 shows the results from the UV/Vis spectroscopy of the films of neat TPS and TPS reinforced with CNF, TEMPO-oxidized fibers, and BLWF. From Figure 8, it can be seen that the light transmittance of the neat TPS films was very high, and it was reduced greatly with the addition of cellulose fibers. The TPS reinforced with 10% CNF had the highest transparency of the composite films. The films with 10% of TEMPO-oxidized fibers and BLWF had very similar transparencies, indicating that these films contain more nonfibrillated cellulose fibers than the film with CNF. The large difference in the transparency of the neat TPS film and the composites can also be partly explained by the fact that the neat TPS film had a very smooth surface in comparison with the films reinforced with cellulose fibers, thus reducing the scattering of light and increasing the light transmittance. Also, it should be noted that even though the specimens used in testing had uniform thicknesses, even small variation in the film thickness may affect the transparency results.

The transparency of the TPS and TPS/cellulose fiber films was also examined visually against a background image, as shown in Figure 9. From Figure 9, it can be seen that all the films are

nearly transparent, despite the fact that the reinforcement is not in nanoscale in materials containing TEMPO-oxidized and BLWF. In addition, no visible aggregates of cellulose fibers or nanofibers could be seen in any of the films. The visual transparency was slightly lower in the case of TPS reinforced with BLWF [Figure 9(d)] and TEMPO-oxidized fibers [Figure 9(c)] when compared to the film reinforced with CNF [Figure 9(b)].

### Moisture Uptake

The effect of different types of cellulose fibers on the moisture absorption of the TPS was determined by placing the specimen in 98% RH, and measuring the moisture uptake after 17 and 30 days. The results from the moisture uptake analysis are shown in Figure 10. As it can be seen from Figure 10, after 17 days



**Figure 10.** Moisture uptake of the neat TPS and TPS reinforced with different types of cellulose fibers after 17 and 30 days in 98% RH. The same letters on top of the columns indicate that the means are not significantly different at 5% significance level based on the ANOVA and Tukey–Kramer pairwise comparison test. The results after 17 and 30 days were analyzed separately.

there were no significant differences in the moisture uptake of the materials. However, after 30 days in 98% RH, the film with TEMPO-oxidized fibers had higher moisture uptake when compared to the other composite films. The reason for this behavior is the hydrophilic carboxylate groups in the surfaces of the TEMPO-oxidized fibers. From Figure 10, it can also be seen that the addition of cellulose fibers did not reduce the moisture absorption of the starch matrix to that extent as it has been reported earlier for TPS reinforced with cellulose fibers/nanofibers.<sup>43,44</sup> Possible explanation for this can be that sorbitol was used as starch plasticizer, which is thought to restrict the moisture uptake of starch more than glycerol due to higher chain length and fewer end hydroxyl groups.<sup>45</sup>

## CONCLUSIONS

In this study, the fibrillation of cellulose fibers into micro or nanosize fibers and the preparation green bionanocomposites in one twin-screw extrusion step was studied. The effect of the processing setup and the fiber type on micro/nanofibrillation and fiber dispersion/distribution in starch was studied. The microscopy studies showed that the nanofibrillation of cellulose fibers was not achieved using these processing conditions. The low viscosity of the starch–fiber mixtures resulting from high water content is the probable reason why the nanofibrillation was not successful. However, the dispersion and distribution of fibers was good in all of the composites, including the composite in which CNF prepared by ultrafine grinding were used indicating that twin-screw extrusion of cellulose nanocomposites can be done in the presence of large amount of water.

The mechanical properties of TPS were enhanced by the addition of cellulose fibers; however, the type of cellulose fiber (BLWF, TEMPO-oxidized fibers, or CNF) did not have any significant effect on the composites' mechanical properties. The light transmittance was lowest for the materials containing BLWF and TEMPO-oxidized fibers, confirming the fact that the fibers were not nanofibrillated during the extrusion. The moisture uptake study showed that the addition of 10 wt % of TEMPO-oxidized fibers increased the moisture absorption of TPS film when compared to the TPS reinforced with other types of cellulose fibers (BLWF and CNF).

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