

Enhancement of nanofibrillation of softwood cellulosic fibers by oxidation and sulfonation



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ABSTRACT

In this study, sulfonic acid groups were introduced to milled softwood (SW) bleached kraft fibers by oxidation and sulfonation with sodium periodate followed by sodium bisulfite under relatively mild conditions. The effect of variable amount of sulfonated groups on nanofibrillation of sulfonated cellulose samples was investigated. The cellulose samples, with contents of sulfonated groups of 371–501 $\mu\text{mol/g}$, were readily nanofibrillated by homogenization at relatively low pressure. These samples converted to viscous and transparent gels without clogging the homogenizer. By passing through the homogenizer one to four times, the transmittances of homogenized suspensions were up to 98%. SEM characterization of the homogenized and lyophilized fibril suspension indicates that the nanofibrillated fibrils are a network structure with lateral sizes of $\sim 15\text{--}45\text{ nm}$ and lengths $> 1\text{ }\mu\text{m}$. The consecutive periodate oxidation and sulfonation with bisulfite was shown to be an effective pretreatment method to facilitate the nanofibrillation of softwood pulp cellulose and can be expectedly used with other cellulosic resources.

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1. Introduction

The demand for environmental friendly products has renewed interest in finding new bio-based materials that are biodegradable and environmentally compatible. Natural cellulosic fibers used as reinforcing elements in polymeric matrices are considered as one of the most promising fillers in preparing sustainable composite materials (Abdelmouleh, Boufi, Belgacem, & Dufresne, 2007; Li, Tabil, & Panigrahi, 2007). In comparison to conventional engineered fibers such as glass and carbon fibers, cellulosic fibers provide many advantages including low density, low cost, renewability, biodegradability, non-abrasive properties, high specific strength and with safer handling properties as compared with synthetic reinforcements as well as a favorable carbon dioxide balance (Besbes, Alila, & Boufi, 2011a; Bledzki & Gassan, 1999; John & Thomas, 2008). Although cellulosic fiber biocomposites are widely used in industry as a low-cost engineered material with several synthetic polymers and concrete, the microstructural heterogeneity and limited aspect ratio of cellulosic fibers causes low strength, and

low strain-to-failure problems (Berglund & Peijs, 2010). As an alternative, high quality cellulose nanofibers isolated from wood pulp fibers have become attractive material for developing new composites. Indeed, cellulose nanocomposites are opening new areas for application in health care, packaging, electronics, the automotive sector, construction and other areas (Oksman, Mathew, & Sain, 2009). Cellulose nanofibers have high aspect ratios, diameters in the 5–15 nm range, and intrinsically superior physical properties including high Young's modulus (138 GPa in the crystalline region along the longitudinal direction) (Nishino, Takano, & Nakamae, 1995), high strength and very low coefficient of thermal expansion (Nishino, Matsuda, & Hirao, 2004). To date, polymer nanocomposites reinforced with cellulose nanofiber networks have been shown to exhibit high strength, high work-of-fracture, and transparency.

There are three primary cellulose nanostructures, nanocrystalline cellulose (NCC) (Yang, Tejado, Alam, Antal, & van de Ven, 2012), nanocellulose balls (Zhang, Elder, Pu, & Ragauskas, 2007) and cellulose nanofibers (CNF) also referred to as microfibrillated cellulose (MFC) (Alila, Besbes, Vilar, Mutje, & Boufi, 2013). NCC and nanocellulose balls are most often prepared by acid hydrolysis of natural cellulosic fibers by sulfuric acid or hydrochloric acid (Araki, Wada, Kuga, & Okano, 1998; Beck-Candanedo, Roman, & Gray, 2005). Cellulose nanofibers or microfibrillated cellulose is typically prepared from wood pulp fibers by high shear mechanical treatments providing a high yield of MFC which were first described by Turbak, Snyder, and Sandberg (1983) two decades ago. One of the

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most prevalent mechanical methods to acquire MFC is a homogenizing process in which a low consistency wood pulp fiber suspension is processed through a high pressure mechanical homogenizer that facilitates the microfibrillation of pulp fibers (Nakagaito & Yano, 2004).

Although MFC exhibits a high potential for numerous applications, the one major challenge that needs to be addressed before considering real-world applications is developing a low-energy microfibrillation process. In pulp fibers, the nanofibrils are packed together tightly by hydrogen bonding and London forces (Keckes et al., 2003). So far, most existing methods for microfibrillation require a considerable amount of mechanical energy to disrupt the fiber wall (Tejado, Alam, Antal, Yang, & van de Ven, 2012). Therefore the efficient production of nanofibrils on a large scale is challenging in terms of production cost, capacity, and quality (Liimatainen, Visanko, Sirvio, Hormi, & Niinimäki, 2012).

To facilitate the microfibrillation of natural cellulose fibers, the use of enzymatic or chemical pretreatments on cellulose fibers has become popular with the aim of reducing the amount of mechanical energy needed. One effective method to lower mechanical energy costs is to introduce negatively charged carboxylate groups (COO^-) on cellulose microfibrils surface to establish repulsive forces under mild alkaline condition between microfibrils, which facilitates the separation, and stability of these microfibrils. Saito and Isogai researched the microfibrillation of hardwood bleached kraft pulp fibrils using 2,2,6,6-tetramethylpiperidine-1-oxyl radical catalyst (TEMPO–NaClO–NaClO₂) under neutral conditions to selectively convert the primary hydroxyl groups of cellulose on fibril surface to carboxylate groups. The results show that as the carboxylate content on the fibril reached 780 $\mu\text{mol/g}$, the fiber was easily mechanically fibrillated and dispersed in water as individual fibrils using a domestic blender followed by sonicating using an ultrasonic homogenizer (Saito & Isogai, 2004). Besbes et al. studied the oxidation effect of TEMPO–NaBr–NaClO–NaClO₂ system under neutral condition on the nanofibrillation of commercial bleached eucalyptus, pine kraft pulp, and Alfa fibers that were treated by 15% NaOH solution (v/v). As the carboxyl content approached 500 $\mu\text{mol/g}$, the eucalyptus and pine fibers were easily fibrillated, with a yield in nanosized fibrils exceeding 90% after several passes through homogenizer at 60 MPa, while treated Alfa fibers exhibited higher resistance to the fibrillation process which they ascribed to the higher degree of crystallinity for Alfa fibers (Besbes, Vilar, & Boufi, 2011b). The above oxidation system also facilitated the microfibrillation of fibers pulped from non-woody plants using a homogenizer operating under a pressure of less than 60 MPa, reported by Alila et al. (2013), the yielded fibrils were of width of 20 to 50 nm, depending on the fiber origin. Takaichi and Isogai reported recently that softwood bleached kraft pulp was oxidized with 2-azaadamantane *N*-oxyl (AZADO) or 1-methyl-AZADO in a NaBr/NaClO system in water at pH 10. Compared to TEMPO/NaBr/NaClO system, the oxidation time needed for the preparation of oxidized celluloses with carboxylate contents of 1.2–1.3 mmol/g was reduced from ~80 to 10–15 min, and the needed molar amounts of AZADO and 1-methyl-AZADO was just 1/32 and 1/16 of the amount of TEMPO added, respectively. The AZADO oxidized wood cellulose, which had a carboxylate content of 1.2 mmol/g, was mechanically disintegrated in water, an almost transparent dispersion obtained, with a nanofibrillation yield of 89% (Takaichi & Isogai, 2013).

In summary, the above research based on the TEMPO oxidation system, oxidized the primary hydroxyl groups of cellulose, and typically yielded a carboxyl content of 500 $\mu\text{mol/g}$ to 780 $\mu\text{mol/g}$. However, the TEMPO oxidation route involves reaction conditions which are difficult to scale-up to an industrial level and TEMPO-mediated oxidation alone cannot cause spontaneous break up of fibers into nanofibrils, as pointed out by Alam, Tejado,

Antal, and van de Ven (2010). Furthermore, they reported a novel route to prepare nanofibrillar cellulose (NFC) from softwood kraft pulp cellulose fibers that for the first time does not require the application of large amounts of mechanical shear or ultrasonics. This purely chemical method introduced a high number of charge groups in cellulose, which weakens the structure due to the appearance of repulsive forces and results in the spontaneous break-up of the fibers into nanofibrils. This novel route includes two steps. First, the cellulose was oxidized by periodate followed by chlorite to convert C2 and C3 hydroxyl groups to dicarboxyl groups with the content up to 2500 $\mu\text{mol/g}$. The oxidized cellulose was then further treated with a TEMPO-mediated oxidation converting primary hydroxyl groups on cellulose C6 to the carboxyl groups yielding a total content of charged carboxyl groups of up to 3500 $\mu\text{mol/g}$. The produced di- and tricarboxylated cellulose nanofibrils have a high aspect ratio and are about three times larger in charge densities than NFCs produced by TEMPO oxidation. More recently, Liimatainen et al. employed sequential periodate and chlorite oxidation as an efficient pretreatment to enhance nanofibrillation of hardwood cellulose pulp through homogenization. The results show that as carboxyl contents reach values ranging from 380 to 1750 $\mu\text{mol/g}$, the bleached hardwood (birch) chemical pulp cellulose fiber could be nanofibrillated to a highly viscous and transparent gel with yields of 100–85% without clogging the homogenizer using one to four passes. SEM characterization shows the obtained nanofibrils were of typical widths of approximately 25 ± 6 nm (Liimatainen et al., 2012). From these research studies, it can be seen that it is the carboxylic group imparts negative charge and the resulting repulsive forces between microfibrils facilitates microfibrillation and stability of these nanostructures.

In comparison, the sulfonic acid group has a stronger acidity than carboxylic acid group as the acid dissociation constant pK_a is ~1 for sulfonic acid whereas organics acids have a pK_a of 3–5. Hence, it could be reasonably inferred that if sulfonic acid groups were introduced into cellulose, it would readily lead to microfibrillation. Indeed, the oxidation/sulfonation of cellulose has been studied by several researchers. Shet (1995) modified cellulose pulp by first oxidizing cellulose with sodium periodate followed by sulfonation with sodium bisulfite. The pulps used included samples derived from both woody and nonwoody plants by kraft and/or soda pulping followed by chemical bleaching. The results showed that sulfonation of the cellulose fiber in the range of 0.01–0.04 sulfonate groups/per glucose unit in cellulose significantly increased dry and wet tensile strength as well as the ratio of wet strength to dry strength. Therefore, this modified cellulose fiber is extremely useful in a wide variety of paper products that require a combination of good strength in both wet and dry applications. Similar research by Hou, Liu, Liu, and Bai (2007) demonstrated that a bleached kraft softwood pulp fibers after periodate oxidation followed by sulfonation exhibited not only improved fiber water absorbency and fiber swelling property but also increased dry and rewet tensile strengths. Zhang, Jiang, Dang, Elder, and Ragauskas (2008) investigated the effect of oxidation and sulfonation on the chemical and physical properties of bleached hardwood kraft pulp and derived nanocellulosic whiskers and cellulose nanospheres. It was found that the water absorbency of the modified cellulosic materials can be enhanced by 8.0–199.0% with this oxidation/sulfonation protocol. Analogous research was performed by Rajalaxmi et al. which showed a fraction of periodate oxidized/sulfonated pulp became soluble in water as measured by ^1H NMR (Rajalaxmi, Jiang, Leslie, & Ragauskas, 2010). More recently, Liimatainen, Visanko, Sirvio, Hormi, and Niinimäki (2013) reported that the hardwood pulp was converted to nanofibrils with sulfonated functionality through a homogenizer by consecutive pre-treatment of cellulose with periodate and

bisulfite. As the sulfonated celluloses having the anionic charge densities of 0.18–0.51 mmol/g, the nanofibrils (with typical widths of 10–60 nm) were obtained by high pressure homogenization without use of any mechanical pre-treatment (Liimatainen et al., 2013).

In this paper, nanofibrils with sulfonic acid groups were acquired from Wiley milled softwood bleached kraft fibers through homogenization. Sulfonated groups were introduced onto fibrils by periodate oxidation and sulfonation with bisulfite at room temperature. Aldehydes in starting and oxidized fibers were analyzed by copper number determination and FT-IR spectroscopy. Sulfonated fibers were purified by dialysis and centrifugation and analyzed by conductometric titration. Homogenized sulfonated nanofibrils were characterized by optical transmittance measurement and field-emission scanning electron microscopy. The effect of variable amount of sulfonated groups on nanofibrillation of sulfonated cellulose samples was investigated.

2. Materials and methods

2.1. Materials

A commercial fully bleached softwood kraft pulp acquired from a southeastern U.S. kraft pulp mill was used for all studies in this research. The cellulose, xylan, mannan, galactan, and arabinan contents of the pulp were 82.3, 9.56, 6.43, 0.27, and 0.71%, respectively, which were analyzed according to TAPPI method T 249 using high-performance anion-exchange chromatography with pulsed amperometric detection (Sluiter et al., 2008). The bleached softwood kraft pulp also contained 0.66% acid-soluble lignin and was measured using an UV/vis spectrophotometer (UV160U, Shimadzu) from the absorbance at 205 nm according to Lin and Dence (Lin & Dence, 1992). The bleached softwood kraft pulp fibers were milled with a Wiley mill using a 0.50 mm sieve to yield a uniform short fiber; for the controlled samples the Wiley milled fibers were further fibrillated by PFI beating for 20,000 revolutions. Sodium periodate (NaIO_4 , 99%) was acquired from Aldrich chemical company; all other chemicals were purchased from VWR international and used as received unless otherwise specified.

2.2. Sodium periodate oxidation of pulp fiber cellulose

A suspension of Wiley milled fibers (20.0 g, O.D.) in deionized (DI) water (600 mL) was reacted with sodium periodate (8.0 g, 37.4 mmol) for 24 h with stirring at room temperature in the absence of light. The reacted fiber suspension was then filtered through Whatman no. 4 filter paper and washed repeatedly with DI water to remove spent oxidant, and then dispersed in DI water (~600 mL) to form a uniform suspension. Aliquots of this suspension were freeze-dried for aldehyde group characterization and yield analysis. The same procedure was followed for preparing all the oxidized samples and these samples were named as DAC 0.40, DAC 0.60, DAC 0.80 and DAC 1.00 (DAC = 2,3-dialdehyde cellulose, 0.40, 0.60, 0.80, and 1.00 = mass ratio of NaIO_4 to pulp fiber). To investigate the effect of oxidation on degree of polymerization (DP), the oxidized celluloses samples (0.25 g) were reduced at room temperature for 2 days in an Erlenmeyer flask (125 mL), using NaBH_4 (0.50 g, 13 mmol) in a 0.5 M NaHCO_3 solution; this reduction converted C2/C3-carbonyl groups to hydroxyl groups (Shinoda, Saito, Okita, & Isogai, 2012). Then the reduced samples were filtered and washed thoroughly with DI water followed by freeze-drying. The DPs of the drying samples were measured with the procedures described in our previous work (Pan, Pu, Foston, & Ragauskas, 2013).

2.3. Sulfonation of 2,3-dialdehyde cellulose

The 2,3-dialdehyde cellulose (15.0 g, O.D.) was suspended in DI water (560 mL) and reacted with sodium bisulfite (7.5 g, 72 mmol) at room temperature for 42 h with stirring. The sulfonated fiber suspension was dialyzed against DI water using cellulose acetate membrane (MWCO 12,000) for 10 days, followed by centrifugation at 12,000 rpm and 4 °C for 50 min, re-dispersed the sediment in DI water and centrifugation, this procedure was repeated until the conductivity of the supernatant was $<10 \mu\text{S}/\text{cm}$. The purified sulfonated fibers were re-dispersed in DI water to form 0.30% suspension and an aliquot was freeze dried for sulfonic acid group characterization. All the samples were prepared using the same amount of 2,3-dialdehyde cellulose fiber and sodium bisulfite and referred to as SC 0.40, SC 0.60, SC 0.80, and SC 1.00 (SC = sulfonated cellulose, 0.40, 0.60, 0.80, and 1.00 = mass ratio of NaIO_4 to pulp fiber).

2.4. Determination of carbonyl content of dialdehyde cellulose

The carbonyl content of the dialdehyde cellulose (DAC) was determined by measurement of copper number (Cu no.) based on TAPPI method T 430 with a slight modification. In brief, a mixture of an aqueous CuSO_4 solution (10 mL, 0.40 M) and a sodium carbonate–sodium bicarbonate solution (95 mL, 1.04 M–0.60 M) was heated to 100 °C, then reacted with DAC samples (0.10 g) in a boiling water bath for 3 h, cooled, filtered through no. 40 Whatman ashless filter paper, and washed with 5% NaCO_3 solution (100 mL) and hot water (250 mL) at 95 °C. The filtered samples were transferred to a beaker, and dispersed in 5% phosphomolybdic acid (65 mL), stirred for 5 min with a glass bar, filtered and washed with DI water until the blue molybdenum oxide color disappeared from the DAC sample. The filtrate was diluted with DI water to 700 mL followed by titration with KMnO_4 solution (0.05 N) to a faint pink end point. A blank determination was performed following the same procedure. For each sample, the experiment was repeated two times to obtain the copper number and the data were reported as an average with an error of less than $\pm 1.7\%$.

The copper number was calculated using Eq. (1):

$$\text{copper number} = \frac{[6.36(V - B)N]}{W} \quad (1)$$

where V indicates volume of KMnO_4 solution to titrate the filtrate from the specimen (mL); B , volume of KMnO_4 solution to titrate the blank filtrate (mL); N , normality of KMnO_4 (0.05 N); and W , weight of pulp fibers (g).

2.5. FT-IR characterization of aldehyde group

Fourier transform infrared spectroscopy (FT-IR) was used to characterize the aldehyde groups in DAC samples. Starting fiber, sodium periodate oxidized fiber samples were analyzed with a 100 FT-IR spectrometer from Perkin-Elmer with a universal attenuated total reflection (ATR) accessory. Fiber samples were placed directly on the ATR crystal, and pressed uniformly and tightly against the diamond surface using a spring loaded anvil. FT-IR spectra were obtained by averaging 32 scans from 4000 to 650 cm^{-1} at 4 cm^{-1} resolution in the absorption mode. Baseline and ATR corrections for penetration depth and frequency variations were carried out using the Spectrum One software supplied with the instrument.

2.6. Sulfonic group measurements

The sulfonic acid group content of sulfonated fiber sample was measured by conductometric titration carried out with an EC Meter, model 2052 with cell constant of 10 cm^{-1} based on a

Table 1

The mass yields of oxidized fibers and sulfonated fibers after oxidation and sulfonation.

NaIO ₄ /pulp	0.40	0.60	0.80	1.00
Oxidation yield (%)	94.1	94.4	92.1	91.1
Sulfonation yield (%)	85.3	84.9	80.8	72.3

literature procedure (Katz, Beatson, & Scallan, 1984). Starting fiber and freeze dried oxidized and sulfonated fiber samples (0.30 g) were soaked in HCl solution (60 mL, 0.10 N) with stirring for 1 h, then filtered through a Whatman polyamide membrane filter (0.2 μm) and washed with DI water to remove excess acid until the pH of filtrate was same as DI water. The protonated fibers were dispersed in NaCl solution (75 mL, 0.0006 N), and titrated with a 0.05 N sodium hydroxide solution. Titration was performed under a nitrogen atmosphere with magnetic stirring. With every addition of NaOH solution, the solution conductivity was recorded until a steady state value was acquired.

2.7. Homogenization of fiber samples

Both the control fiber and the oxidized/sulfonated fiber samples were suspended in DI water at a consistency of 0.3%. The suspensions were nanofibrillated using a high-pressure homogenizer (Nano DeBEE, Nano 45 110 V). The suspensions were first passed five times (5p) through a Z8 nozzle with diameter of 0.21 mm and pressure of ~70 MPa, then passed through a Z5 nozzle which had an orifice diameter of 0.13 mm and an applied pressure of ~140 MPa. After every pass, an aliquot of ~15 mL was acquired for the analysis of MFC properties.

2.8. Transmittance measurements

The transmittance of 0.1% nanofibrillated cellulose suspensions was measured between wavelength of 200 and 800 nm with a data interval of 1 nm using a PerkinElmer Lambda 35 UV/vis spectrometer. The spectrum of a spectrophotometer cell filled with DI water was used as blank.

2.9. Field emission scanning electron microscopy (FESEM)

The suspensions of nanofibrillated cellulose (with a solid content of 0.3%) were deposited on polyamide filter membrane and frozen in a -76 °C freezer, and then freeze dried followed by sputter-coated with gold for 30 s after drying (the thickness of gold coat is 5–7 nm). FESEM (LEO 1530) images of the freeze dried and gold coated samples were collected. The accelerating voltage during imaging was 3 kV.

3. Results and discussions

3.1. Effect of reaction conditions on oxidized and sulfonated fiber products

A schematic reaction pathway for oxidation and sulfonation of cellulose is shown in Fig. 1.

Table 1 summarizes the fiber yield after oxidation and sulfonation. It can be seen that as the weight ratio of NaIO₄ to pulp fiber was increased, the oxidized fiber mass yield decreased from 94.1% using a mass ratio of NaIO₄:pulp of 0.40 to 91.1% when using a ratio of NaIO₄:pulp of 1.00. This was tentatively ascribed to a peeling reaction of cellulose and possibly some degraded cellulose/hemicellulose fragments dispersed in solution that could not be recovered. The yield of sulfonated fiber was also decreased as the weight ratio of NaIO₄:pulp was increased. When the weight ratio of

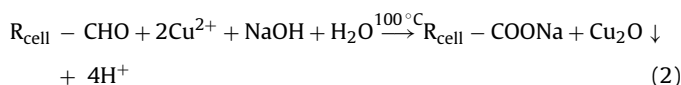
Table 2

Copper number and carbonyl group content of oxidized cellulosic fibers.

Samples	NaIO ₄ /pulp fiber (w/w)	Copper number (g of Cu/100 g fiber)	Carbonyl content (mmol/g)
Starting fiber	0	0.53	0.01
DAC 0.40	0.40	40.3	0.67
DAC 0.60	0.60	66.4	1.11
DAC 0.80	0.80	85.8	1.43
DAC 1.00	1.00	95.3	1.59

NaIO₄:pulp was 1.00, the yield of sulfonated fiber was 72.3%, which is comparable to the yield of 63% reported by Yang et al. (2012) in their work in which the hydroxyl groups in cellulose were converted to carboxyl groups by periodate/chlorite oxidation followed by TEMPO mediated oxidation.

The carbonyl group content in dialdehyde cellulose (DAC) after oxidation by sodium periodate was determined by measurement of copper number (Cu no.) of DAC samples. The copper number determination is based on the reduction of copper(II) ion (CuSO₄) to copper(I) by cellulosic aldehyde groups in a hot, alkaline medium as shown in Eq. (2) (Morgan & Henry, 1959). The quantity of formed Cu₂O is chemically equivalent to the groups oxidized in the cellulose. The copper number is expressed as the number of grams of copper(I) formed on reduction of copper(II) with 100 g cellulose. The carbonyl group content of DAC samples was calculated using Eq. (3) (Rohrling et al., 2002).



$$\text{carbonyl group content} \left(\frac{\text{mmol}}{100 \text{ g}} \right) = \frac{(\text{Cu no.} - 0.07)}{0.6} \quad (3)$$

The data in Table 2 shows the effect of weight ratio of sodium periodate to SW cellulosic fiber on the copper number (Cu no.) and carbonyl group content. It can be seen that as the ratio of sodium periodate to SW cellulosic fiber was increased, the carbonyl group content of oxidized fiber also increased. The content of carbonyl group ranged from 0.67 to 1.59 mmol/g, which are comparable to the data reported by Liimatainen et al. (2012), in their work, the carbonyl group content ranged from 0.36 to 1.68 mmol/g as the bleached birch chemical wood pulp was oxidized with sodium periodate in different conditions.

The oxidation of the SW cellulose fibers can also be detected by FT-IR, the spectra data for the starting SW cellulose fiber and the fibers oxidized by sodium periodate are shown in Fig. 2. In these spectra, the absorption band around 1730 cm⁻¹ corresponds to the carbonyl function group (C=O) stretching frequency of aldehyde groups located on C2 and C3 positions (Fan, Lewis, & Tapley, 2001). The band is absent in the starting fiber sample (spectrum 2a). It can be seen that as the weight ratio of NaIO₄ to pulp was increased, the intensity of this band increased, a maximum value of this band is reached shown in the spectrum Fig. 2e, corresponding to the maximum weight ratio of NaIO₄ to pulp fiber (DAC 1.00). The morphological features of the fibers following periodate oxidation were previously shown to swell the fibers (Rajalaxmi et al., 2010).

The DP_w value for starting pulp cellulose is 2523. After sodium periodate oxidation, the DP_w values for oxidized cellulose samples DAC 0.40, DAC 0.60, DAC 0.80 were 1243, 981, and 592, respectively. The sample DAC 1.00 (20.0 mg) still retained some very small particles after 2 days derivatizing reaction using anhydrous pyridine (5.70 mL) and phenyl isocyanate (0.70 mL), while other samples were thoroughly dissolved converting to tricarbanilates. Therefore, DP_w was calculated up to DAC 0.80. The results indicated that as the ratio of NaIO₄:pulp was increased, the depolymerization

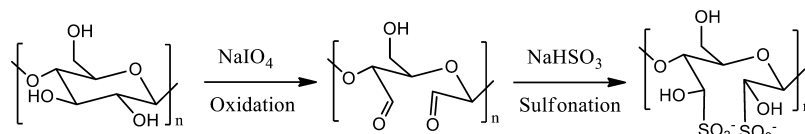


Fig. 1. Sodium periodate oxidation and sodium bisulfite sulfonation of cellulose.

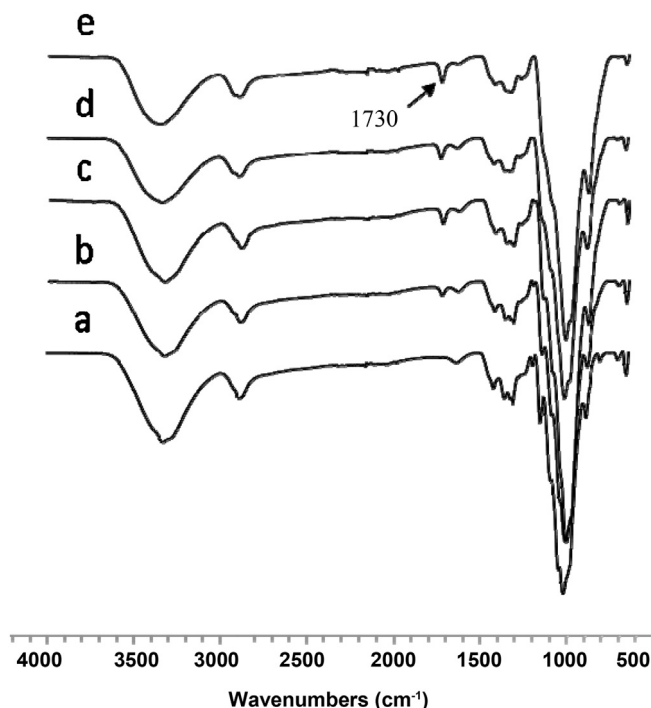


Fig. 2. FT-IR spectra of (a) starting SW cellulose, (b) DAC 0.40, (c) DAC 0.60, (d) DAC 0.80, (e) DAC 1.00 samples.

of cellulose was intensified, the degree of polymerization of cellulose decreased by 50.7, 61.1, and 76.5% as the ratio of NaIO_4 /pulp increased from 0.40 to 0.80, respectively. These data are significant for further applications to films or composites.

It was reported that the periodate oxidation and sulfonation of bleached kraft birch pulp didn't change the crystalline structure of cellulose I to another crystalline form, while the crystalline indexes (CrI) decreased (Liimatainen et al., 2013). This may indicate that some cellulose molecules in crystalline regions were oxidized as well and the DP_w of cellulose was decreased.

The dialdehyde cellulosic fibers were then treated with sodium bisulfite to yield the corresponding sulfonated cellulosic fibers. The sulfonic acid group content in sulfonated fiber samples was determined by conductometric titration and these results are summarized in Table 3. The data in Table 3 indicates that the sulfonic acid group content of the sulfonated fibers increased as the weight ratio of sodium periodate to pulp fibers, from 0 to 501 $\mu\text{mol/g}$. The contents of sulfonic group for the sulfonated fibers are lower than carbonyl group content of corresponding DAC samples, which indicates that not all of carbonyl groups in DAC samples were converted

to sulfonic acid groups in the experimental conditions examined, leaving some carbonyl groups unreacted. These results are comparable to reported by Liimatainen et al. (2013), in their work only 15–30% of aldehydes were converted to sulfonated groups during the bisulfite treatment, while an explanation for this difference was not given. They stated that the high amount of residual aldehydes could cause depolymerization of cellulose chain by β -alkoxy fragmentation. We inferred that the aldehydes could not thoroughly convert to sulfonated groups is likely due in some extent to the repulsion of anionic groups on the cellulose chain, the generated negatively charged sulfonic groups would hinder the adjacent aldehyde groups to be sulfonated due to the static repulsion and steric hindrance.

The conversion of dialdehydes to sulfonated groups exhibited a significant change in fiber surface morphology as they became shorter and exhibited a smoother surface (Rajalaxmi et al., 2010).

3.2. Homogenization of oxidized and sulfonated fibers

To avoid plugging of the homogenizer, the bleached softwood kraft pulp fibers, before oxidation and sulfonation, were milled with a Wiley milling through a 0.50 mm sieve, it was also believed that this process increases the cross-section area of the fiber to facilitate fibrillation (Andresen et al., 2007). All oxidized and sulfonated pulp fiber samples were successfully homogenized without clogging of the homogenizer at a consistency of 0.3% water suspension. As a comparison, Wiley milled unoxidized starting fiber after PFI mill refining for 20,000 revolutions was also homogenized. It should be noted that the Wiley milled unoxidized starting fiber sample couldn't be homogenized, because the fiber sample suspension formed a sediment fiber pad very quickly in sample reservoir and blocked the entrance of the homogenizer. After PFI mill beating for 20,000 revolutions, the unoxidized starting fiber formed a relatively stable suspension and be homogenized.

Fig. 3 shows the appearance of the acquired nanofibrillated cellulose (NFC) gel at 0.3% consistency from the starting unoxidized fiber and oxidized/sulfonated SW pulp fiber samples at different stages of the homogenization process. In Fig. 3, the caption like 5p70M + 5p140M denotes five passes at 70 MPa plus five passes at 140 MPa, and 2p70M means two passes at 70 MPa, etc. For the control unoxidized sample, homogenization was performed at a pressure of 70 MPa for 5 passes followed at higher pressure 140 MPa for up to 20 passes. It seems that this material was not easily nanofibrillated, though the fibers were PFI beaten for 20 K revolutions. The viscous appearances of these homogenized unoxidized control samples are opaque even when homogenized at 140 MPa for 25 passes. The opaque appearance of homogenized unoxidized control samples suggests that the microfibrils in fiber were not individualized and separated but remained agglomerates.

The homogenization of oxidized and sulfonated fiber sample was much easier to accomplish than the unoxidized control sample. For the sample SC 0.40 (NaIO_4 /pulp = 0.40) with sulfonic acid group content of 121 $\mu\text{mol/g}$, five passes at pressure of 70 MPa didn't microfibrillate the pulp fibers as the treated fiber slurry still settled. With additional homogenization at 140 MPa from 5 to 15 passes, the amount of sediment fraction gradually decreased, though the final suspension at 140 MPa for 15 passes was not transparent, the

Table 3
Sulfonic acid group content in oxidized and sulfonated pulp fibers.

Samples	Sulfonic acid group content ($\mu\text{mol/g}$)
Starting fiber	0
SC 0.40	121
SC 0.60	243
SC 0.80	371
SC 1.00	501

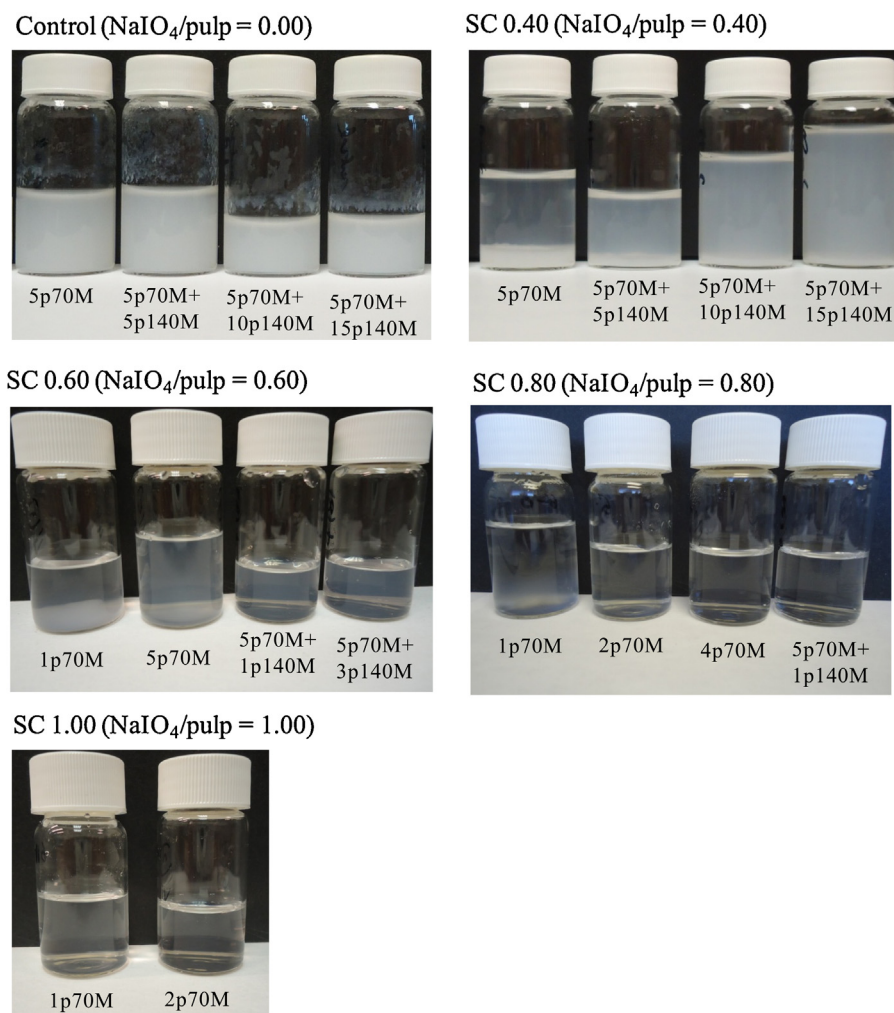


Fig. 3. Appearance of homogenized NFC gels at 0.3% consistency issuing from oxidation by different weight ratio of NaIO_4 /pulp fiber followed by sulfonation treatment.

supernatant fraction became more translucent and the suspension system was stable.

As sulfonic acid group contents of the fiber samples increased, the nanofibrillation became easier. For example, sample SC 0.60 (NaIO_4 /pulp=0.60) with a sulfonic acid group content of $243 \mu\text{mol/g}$, when treated with five passes in homogenizer at a pressure of 70 MPa converted the fibrous sample to a viscous near-transparent suspension system, one additional pass at a pressure of 140 MPa yielded a transparent suspension. Further increasing the sulfonic acid content to $371 \mu\text{mol/g}$ in fiber sample of SC 0.80 (NaIO_4 /pulp=0.80) yielded a fibrous sample that could be converted to transparent system using two passes in homogenizer at a pressure of 70 MPa. When the sulfonic acid content was increased to $501 \mu\text{mol/g}$ in fiber sample from SC 1.00 (NaIO_4 /pulp = 1.00), only one pass in homogenizer at a pressure of 70 MPa was sufficient to nanofibrillate the fiber sample to a viscous transparent suspension system.

3.3. Characterization of nanofibrillated cellulosic suspensions

Fig. 4 shows the transmittance spectra of diluted suspensions (0.1%) of nanofibrillated cellulose samples acquired from oxidation with different weight ratio of NaIO_4 /pulp followed by sulfonation and homogenization. These transmittance spectra were acquired in the range of 200–800 nm, which provided further evidence of the effect of oxidation and sulfonation on the

homogenization and transparency of the nanofibrillated cellulose suspension. For the control unoxidized pulp sample, the transmittance increases as the homogenization was performed, overall the transmittance of the suspensions is low, the highest transmittance at 800 nm is lower than 30% for the sample which was homogenized 5 passes at 70 MPa followed additional 15 passes at 140 MPa. This effect can be likely attributed to the presence of the non-fibrillated fibers or re-agglomerated microfibrillated fibrils responsible for the light-scattering result.

For sample SC 0.40 (NaIO_4 /pulp = 0.40) with sulfonic acid group content of $121 \mu\text{mol/g}$, the transmittance of the sample suspensions increased compared to the control sample at the same homogenization condition. While the transmittance is still low, it is 54% at 800 nm for the sample that was homogenized 5 passes at 70 MPa followed additional 15 passes at 140 MPa. These results may indicate that the limited amount ($121 \mu\text{mol/g}$) of sulfonic acid groups was not enough to establish the repulsive force needed between the microfibrils and hence, the ability to facilitate the microfibrillation of pulp fibers is limited.

As the sulfonic acid group content was increased to $243 \mu\text{mol/g}$ for the sample SC 0.60 (NaIO_4 /pulp=0.60), the transmittance of homogenized cellulose suspension at 800 nm reached 48% with one pass in the homogenizer with a pressure of 70 MPa, five passes at this pressure offer 90% transmittance, one additional pass at the pressure of 140 MPa (5p70M + 1p140M) yielded almost a transparent solution (i.e., 96% transmittance). When this material was

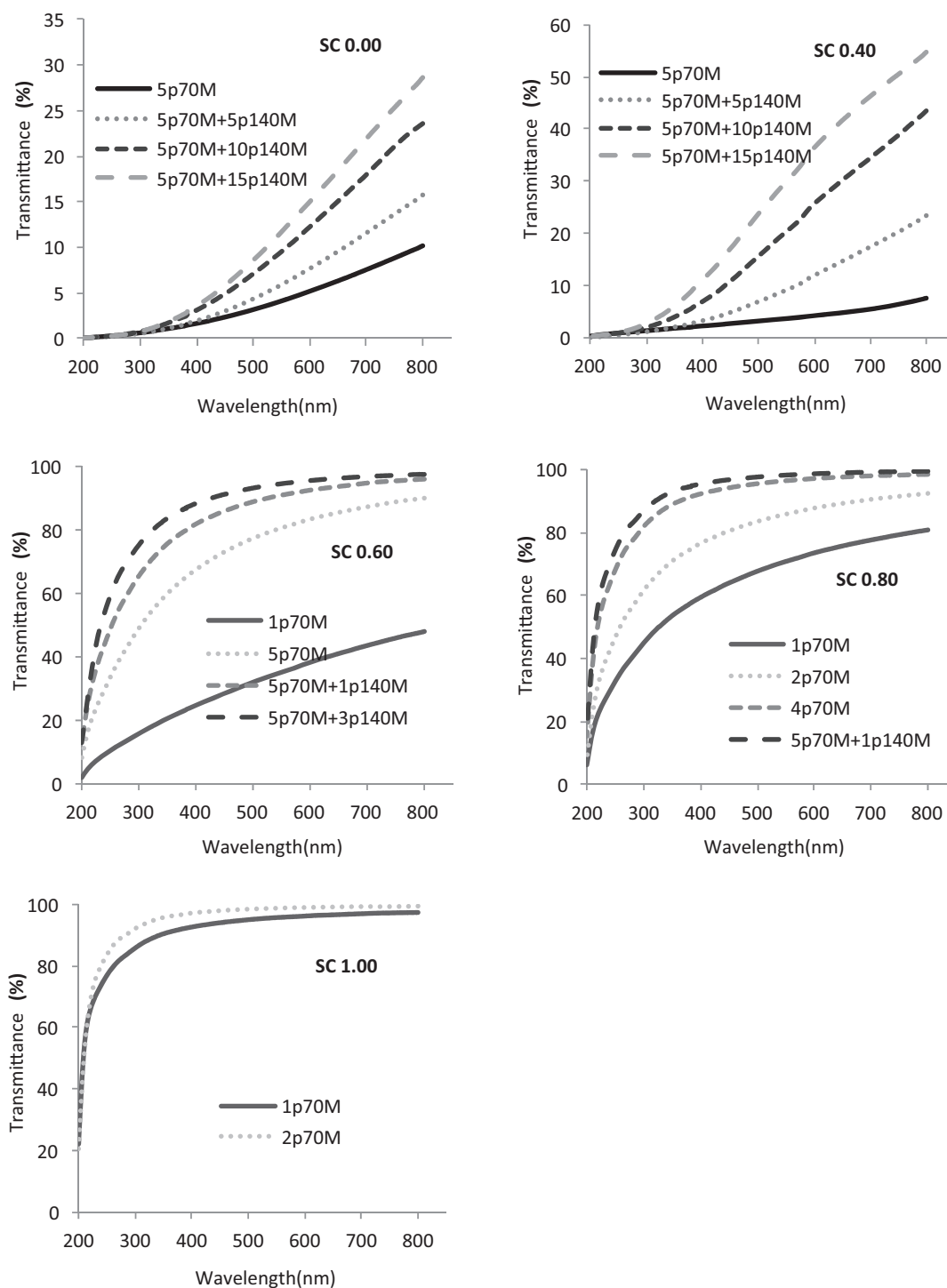


Fig. 4. The UV/vis transmittance spectra of diluted suspensions (0.1%) of nanofibrillated fiber samples oxidized with different weight ratio of NaIO_4 /pulp followed by sulfonation and homogenization in different stages.

treated to another two more passes at a pressure of 140 MPa (5p70M+3p140M) the transmittance of the nanocellulosic material increased from 96 to 98%, while the transmittance at 400 nm increased from 82 to 89% indicating that high pressure homogenization further individualizing the nanofibrils.

Further increasing the sulfonic acid group content to 371 $\mu\text{mol/g}$ for the sample SC 0.80 (NaIO_4 /pulp = 0.80) makes the homogenization even easier, with transmittance of nanocellulosic suspension reaching 81% at 800 nm and 59% at 400 nm using one pass through homogenizer at the pressure of 70 MPa, two passes

at this pressure yielded a suspension transmittance of 92% at 800 nm and 76% at 400 nm. Two more passes through the homogenizer at this pressure (4p70M) yielded transmittance of 98% at 800 nm and 92% at 400 nm. Another pass at this pressure plus one pass at higher pressure (5p70M+1p140M) increased slightly the transmittance to 99% at 800 nm and 95% at 400 nm. These results indicate that at higher content of sulfonic acid groups, the fiber sample can be easily nanofibrillated to form stable nanocellulosic fibrils system at relatively lower pressure homogenization.

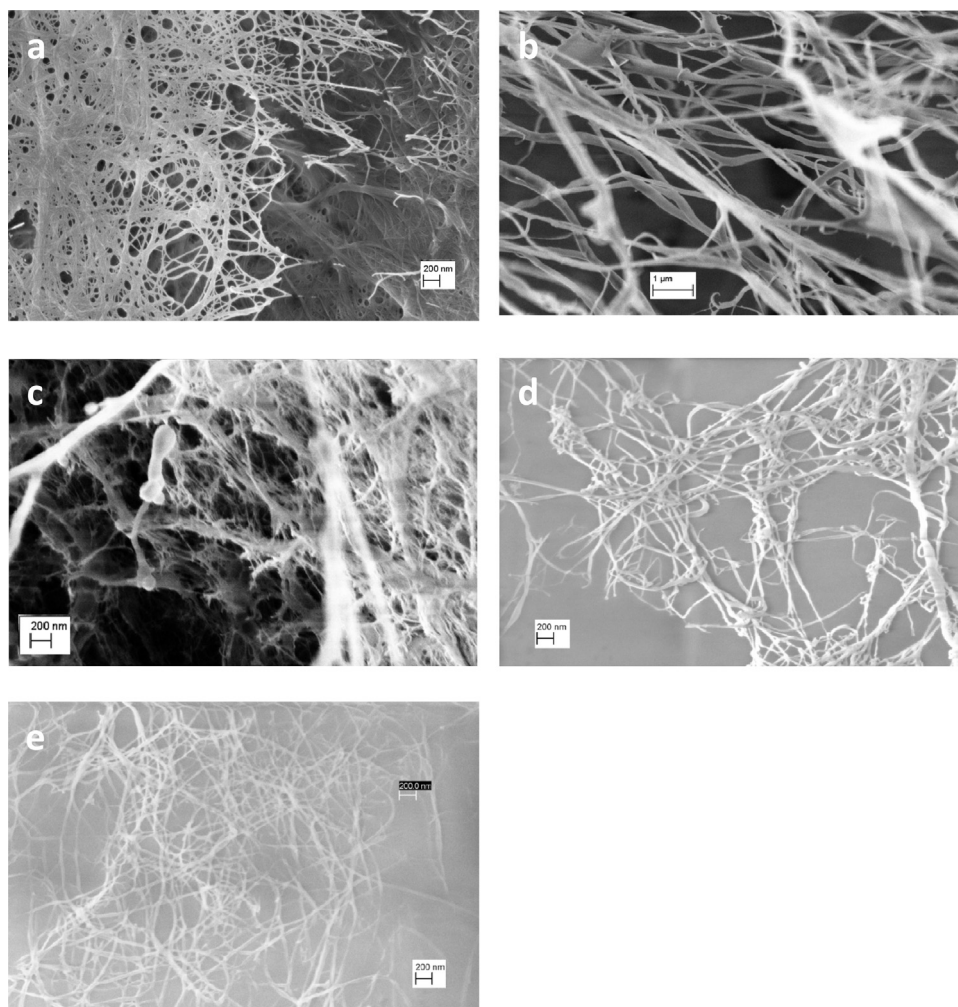


Fig. 5. FE-SEM images of homogenized cellulosic fibrils from the starting unoxidized sample 5p70M + 15p140M (a) and samples of SC 0.40, 5p70M + 15p140M (b), SC 0.60, 5p70M + 1p140M (c), SC 0.80, 2p70M (d) and SC 1.00, 1p70M (e).

Finally, as the sulfonic acid group content was further increased to 501 $\mu\text{mol/g}$ for the sample SC 1.00 ($\text{NaIO}_4/\text{pulp} = 1.00$), just one pass at the pressure of 70 MPa was enough to homogenize the fiber sample to get very high transmittances of 97% at 800 nm and 92% at 400 nm. These effects were attributed to the repulsive properties of the deprotonated sulfonic acid groups introduced on the microfibrils that facilitate the separation of the microfibrils in the homogenization process, and help stabilize nanofibrillar cellulose structures in suspension thereby hindering re-aggregation phenomena. The apparently transparent dispersion of homogenized sulfonated sample SC 1.00 (2p70M) was characterized by qualitative solution-state ^{13}C NMR. The homogenized cellulose suspension (0.3%) was transferred into a 5 mm NMR tube and the NMR spectrum was acquired at room temperature using an insert containing $\text{DMSO}-d_6$ as the lock solvent, running with a Bruker Avance-III 400-MHz spectrometer operating at a frequency of 100.59 MHz for ^{13}C . Over 10,000 scans were collected with a pulse delay of 1.0 s. The result showed that the transparent dispersions consisted of nanofibrillated celluloses alone without any oxidized cellulose molecules dissolved in water at the molecular level.

Based on Figs. 3 and 4 and the discussion above, it can be concluded that the starting unoxidized SW pulp fibers could not be nanofibrillated under the experimental conditions examined whereas the introduction of sulfonic acid groups to cellulosic SW pulp fiber facilitated the nanofibrillation of pulp fibers. In general, the higher the sulfonic acid group content in the SW pulp fibers,

the higher negative charge was imparted, and the easier the pulp fibers were nanofibrillated and less possibility of the aggregation of the nanofibrils in the suspension. As the content of sulfonic acid groups ranged from 371 $\mu\text{mol/g}$ to 501 $\mu\text{mol/g}$, the fibers could be nanofibrillated to a viscous and transparent nanocellulosic suspension (the transmittance up to 98%) by one to four passes in the homogenizer at a relatively lower pressure without clogging the homogenizer. Our data are comparable to the results reported by Besbes et al. (2011a,b) that as the carboxyl content was brought up to 500 $\mu\text{mol/g}$, the eucalyptus and pine fibers were more easily fibrillated; and to results by Liimatainen et al. (2012) that as the carboxyl contents reach ranging from 380 to 1750 $\mu\text{mol/g}$, the hardwood cellulose pulp could be nanofibrillated to highly viscous and transparent gels. The charge functional group (sulfonic acid) content (371–501 $\mu\text{mol/g}$) is relatively lower for our sulfonated fibers to be successfully nanofibrillated than the carboxyl group content of 780 $\mu\text{mol/g}$ for individualization of nano-sized hardwood bleached kraft pulp cellulose fibrils conducted by Saito et al. (2009) and the carboxyl group content of 2500–3500 $\mu\text{mol/g}$ to prepare nanofibrillar cellulose (NFC) from wood cellulose fibers reported by Yang et al. (2012).

Fig. 5 shows the SEM images of homogenized cellulosic fibrils from the starting unoxidized sample, 5p70M + 15p140M (a), samples of SC 0.40, 5p70M + 15p140M (b), SC 0.60, 5p70M + 1p140M (c), SC 0.80, 2p70M (d) and SC 1.00, 1p70M (e). It can be seen that for starting unoxidized fiber sample (5a), the fibers were

not thoroughly microfibrillated after 5 passes at 70 MPa plus 15 passes at 140 MPa. Under the same homogenizing conditions as used for starting sample, SC 0.40 sample (sulfonic acid group content of 121 $\mu\text{mol/g}$) could be homogenized to form thick fibrils (5b). As the sulfonic acid content was increased to 243 $\mu\text{mol/g}$ for sample SC 0.60 (5c), the fibers could be nanofibrillated by five passes at 70 MPa plus one pass at 140 MPa, while the nanofibrillated fibrils still have the trend to form agglomerates. Whereas as the sulfonic acid contents reached to 371 $\mu\text{mol/g}$ for sample SC 0.80 (5d) and 501 $\mu\text{mol/g}$ for sample SC 1.00 (5e), the fibers could be nanofibrillated to form stable nanocellulose fibrils with lateral size of 15–45 nm and the length of $>1\ \mu\text{m}$. Since sample SC 1.00 contains a higher amount of sulfonic acid groups than SC 0.80, the nanocellulosic fibrils for SC 1.00 seemed a little thinner and forming more uniform networks than that from sample SC 0.80. Our SEM images of homogenized nanocellulosic fibrils are similar to the results of nanofibrillated cellulose homogenized from softwood pulps derived from sulfite pulping processes summarized by Khalil, Bhat, and Yusra (2012) and nanofibrillated cellulose of bleached birch chemical wood pulp which was obtained by sequential periodate–chlorite oxidation followed by homogenization, reported by Liimatainen et al. (2012).

4. Conclusions

This paper presents the enhancement of nanofibrillation of an ECF bleached softwood kraft pulp by oxidation and sulfonation followed by homogenization. The sulfonated SW pulp fiber samples were prepared by sodium periodate oxidation followed by sulfonation with sodium bisulfite in the relative mild conditions compared to the TEMPO mediated chlorite oxidation system. The sulfonic acid group content in fibers increased as the weight ratio of sodium periodate to pulp fiber was increased. Starting unoxidized SW pulp fibers could not be nanofibrillated under the experimental conditions used. If the content of sulfonic acid groups introduced to fiber reached 243 $\mu\text{mol/g}$, the oxidized and sulfonated fibers were easily nanofibrillated. As the content of sulfonic acid groups reached ranging 371 to 501 $\mu\text{mol/g}$, the fibers could be nanofibrillated to viscous and transparent gels (the transmittance up to 98% at 800 nm) just by one to four passes at relatively lower pressure without clogging the homogenizer. The SEM characterization showed that the nanocellulosic fibers are of website network structure with lateral sizes of $\sim 15\text{--}45\ \text{nm}$ and the length $>1\ \mu\text{m}$.

References

- Abdelmouleh, M., Boufi, S., Belgacem, M. N., & Dufresne, A. (2007). Short natural-fibre reinforced polyethylene and natural rubber composites: Effect of silane coupling agents and fibres loading. *Composites Science and Technology*, 67(7–8), 1627–1639. <http://dx.doi.org/10.1016/j.compscitech.2006.07.003>
- Alam, M., Tejado, A., Antal, M., & van de Ven, T. G. (2010). Purely chemical production of nanofibrillated cellulose. Part 2: Getting rid of TEMPO. In *Paper presented at the Pacificchem 2010, international chemical congress of pacific basin societies Honolulu, HI*.
- Alila, S., Besbes, I., Vilar, M. R., Mutje, P., & Boufi, S. (2013). Non-woody plants as raw materials for production of microfibrillated cellulose (MFC): A comparative study. *Industrial Crops and Products*, 41, 250–259. <http://dx.doi.org/10.1016/j.indcrop.2012.04.028>
- Andresen, M., Stenstad, P., Moretro, T., Langsrud, S., Syverud, K., Johanson, L. S., & Stenius, P. (2007). Nonleaching antimicrobial films prepared from surface-modified microfibrillated cellulose. *Biomacromolecules*, 8(7), 2149–2155. <http://dx.doi.org/10.1021/bm070304e>
- Araki, J., Wada, M., Kuga, S., & Okano, T. (1998). Flow properties of microcrystalline cellulose suspension prepared by acid treatment of native cellulose. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 142(1), 75–82. [http://dx.doi.org/10.1016/S0927-7757\(98\)00404-X](http://dx.doi.org/10.1016/S0927-7757(98)00404-X)
- Beck-Candanedo, S., Roman, M., & Gray, D. G. (2005). Effect of reaction conditions on the properties and behavior of wood cellulose nanocrystal suspensions. *Biomacromolecules*, 6(2), 1048–1054. <http://dx.doi.org/10.1021/bm049300p>
- Berglund, L. A., & Peijs, T. (2010). Cellulose biocomposites-from bulk moldings to nanostructured systems. *MRS Bulletin*, 35(3), 201–207. <http://dx.doi.org/10.1557/mrs2010.652>
- Besbes, I., Alila, S., & Boufi, S. (2011). Nanofibrillated cellulose from TEMPO-oxidized eucalyptus fibres: Effect of the carboxyl content. *Carbohydrate Polymers*, 84(3), 975–983. <http://dx.doi.org/10.1016/j.carbpol.2010.12.052>
- Besbes, I., Vilar, M. R., & Boufi, S. (2011). Nanofibrillated cellulose from Alfa, Eucalyptus and Pine fibres: Preparation, characteristics and reinforcing potential. *Carbohydrate Polymers*, 86(3), 1198–1206. <http://dx.doi.org/10.1016/j.carbpol.2011.06.015>
- Bledzki, A. K., & Gassan, J. (1999). Composites reinforced with cellulose based fibres. *Progress in Polymer Science*, 24(2), 221–274. [http://dx.doi.org/10.1016/S0079-6700\(98\)00018-5](http://dx.doi.org/10.1016/S0079-6700(98)00018-5)
- Fan, Q. G., Lewis, D. M., & Tapley, K. N. (2001). Characterization of cellulose aldehyde using Fourier transform infrared spectroscopy. *Journal of Applied Polymer Science*, 82(5), 1195–1202. <http://dx.doi.org/10.1002/app.1953>
- Hou, Q. X., Liu, W., Liu, Z. H., & Bai, L. L. (2007). Characteristics of wood cellulose fibers treated with periodate and bisulfite. *Industrial & Engineering Chemistry Research*, 46(23), 7830–7837. <http://dx.doi.org/10.1021/ie0704750>
- John, M. J., & Thomas, S. (2008). Biofibres and biocomposites. *Carbohydrate Polymers*, 71(3), 343–364. <http://dx.doi.org/10.1016/j.carbpol.2007.05.040>
- Katz, S., Beatson, R. P., & Scallan, A. M. (1984). The determination of strong and weak acidic groups in sulphite pulp. *Svensk Papperstidn*, 87, R48–R53.
- Keckes, J., Burgert, I., Fruhmman, K., Muller, M., Kolln, K., Hamilton, M., & Fratzl, P. (2003). Cell-wall recovery after irreversible deformation of wood. *Nature Materials*, 2(12), 810–814. <http://dx.doi.org/10.1038/nmat1019>
- Khalil, H. P. S. A., Bhat, A. H., & Yusra, A. F. I. (2012). Green composites from sustainable cellulose nanofibrils: A review. *Carbohydrate Polymers*, 87(2), 963–979. <http://dx.doi.org/10.1016/j.carbpol.2011.08.078>
- Li, X., Tabil, L. G., & Panigrahi, S. (2007). Chemical treatments of natural fiber for use in natural fiber-reinforced composites: A review. *Journal of Polymers and the Environment*, 15(1), 25–33. <http://dx.doi.org/10.1007/s10924-006-0042-3>
- Liimatainen, H., Visanko, M., Sirvio, J., Hormi, O., & Niinimäki, J. (2013). Sulfonated cellulose nanofibrils obtained from wood pulp through regioselective oxidative bisulfite pre-treatment. *Cellulose*, 20(2), 741–749. <http://dx.doi.org/10.1007/s10570-013-9865-y>
- Liimatainen, H., Visanko, M., Sirvio, J. A., Hormi, O. E. O., & Niinimäki, J. (2012). Enhancement of the nanofibrillation of wood cellulose through sequential periodate–chlorite oxidation. *Biomacromolecules*, 13(5), 1592–1597. <http://dx.doi.org/10.1021/bm300319m>
- Lin, S., & Dence, C. (1992). *Methods in lignin chemistry*. Heidelberg, Berlin: Springer.
- Morgan, J. E., & Henry, C. L. (1959). New method for determination of copper number of cellulose: Application to viscose rayon. *TAPPI*, 42(10), 859–862.
- Nakagaito, A. N., & Yano, H. (2004). The effect of morphological changes from pulp fiber towards nano-scale fibrillated cellulose on the mechanical properties of high-strength plant fiber based composites. *Applied Physics. A: Materials Science & Processing*, 78(4), 547–552. <http://dx.doi.org/10.1007/s00339-003-2453-5>
- Nishino, T., Matsuda, I., & Hirao, K. (2004). All-cellulose composite. *Macromolecules*, 37(20), 7683–7687. <http://dx.doi.org/10.1021/ma049300h>
- Nishino, T., Takano, K., & Nakamae, K. (1995). Elastic modulus of the crystalline regions of cellulose polymorphs. *Journal of Polymer Science B: Polymer Physics*, 33(11), 1647–1651. <http://dx.doi.org/10.1002/polb.1995.090331110>
- Oksman, K., Mathew, A. P., & Sain, M. (2009). Novel bionanocomposites: Processing, properties and potential applications. *Plastics Rubber and Composites*, 38(9–10), 396–405. <http://dx.doi.org/10.1179/146580109x12540995045723>
- Pan, S., Pu, Y., Foston, M., & Ragauskas, A. J. (2013). Compositional characterization and pyrolysis of Loblolly pine and Douglas-fir bark. *Bioenergy Research*, 6(1), 24–34. <http://dx.doi.org/10.1007/s12155-012-9223-1>
- Rajalaxmi, D., Jiang, N., Leslie, G., & Ragauskas, A. J. (2010). Synthesis of novel water-soluble sulfonated cellulose. *Carbohydrate Research*, 345(2), 284–290. <http://dx.doi.org/10.1016/j.carres.2009.09.037>
- Rohrling, J., Potthast, A., Rosenau, T., Lange, T., Borgards, A., & Kosma, P. (2002). A novel method for the determination of carbonyl groups in celluloses by fluorescence labeling. 2. Validation and applications. *Biomacromolecules*, 3(5), 969–975. <http://dx.doi.org/10.1021/bm020030p>
- Saito, T., Hirota, M., Tamura, N., Kimura, S., Fukuzumi, H., & Isogai, A. (2009). Individualization of nano-sized plant cellulose fibrils by direct surface carboxylation using TEMPO catalyst under neutral conditions. *Biomacromolecules*, 10(7), 1992–1996. <http://dx.doi.org/10.1021/bm900414t>
- Saito, T., & Isogai, A. (2004). TEMPO-mediated oxidation of native cellulose. The effect of oxidation conditions on chemical and crystal structures of the water-insoluble fractions. *Biomacromolecules*, 5(5), 1983–1989. <http://dx.doi.org/10.1021/bm0497769>
- Shet, R.T. (1995). Sulfonated cellulose pulp and method of preparation. *Brit. UK Pat. Appl. GB 2289695 A* 19951129.
- Shinoda, R., Saito, T., Okita, Y., & Isogai, A. (2012). Relationship between length and degree of polymerization of TEMPO-oxidized cellulose nanofibrils. *Biomacromolecules*, 13(3), 842–849. <http://dx.doi.org/10.1021/bm2017542>
- Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., & Templeton, D. (2008). *Determination of structural carbohydrates and lignin in biomass laboratory analytical procedure*. Golden: National Renewable Energy Laboratory.
- Takaichi, S., & Isogai, A. (2013). Oxidation of wood cellulose using 2-azaadamantane N-oxyl (AZADO) or 1-methyl-AZADO catalyst in NaBr/NaClO system. *Cellulose*, 20(4), 1979–1988. <http://dx.doi.org/10.1007/s10570-013-9932-4>
- Tejado, A., Alam, M. N., Antal, M., Yang, H., & van de Ven, T. G. M. (2012). Energy requirements for the disintegration of cellulose fibers into cellulose nanofibers. *Cellulose*, 19(3), 831–842. <http://dx.doi.org/10.1007/s10570-012-9694-4>

- Turbak, A. F., Snyder, F. W., & Sandberg, K. R. (1983). Microfibrillated cellulose, a new cellulose product: Properties, uses, and commercial potential. *Journal of Applied Polymer Science: Applied Polymer Symposium*, 37, 815–827.
- Yang, H., Tejado, A., Alam, N., Antal, M., & van de Ven, T. G. M. (2012). Films prepared from electrosterically stabilized nanocrystalline cellulose. *Langmuir*, 28(20), 7834–7842. <http://dx.doi.org/10.1021/la2049663>
- Zhang, J. G., Elder, T. J., Pu, Y. Q., & Ragauskas, A. J. (2007). Facile synthesis of spherical cellulose nanoparticles. *Carbohydrate Polymers*, 69(3), 607–611. <http://dx.doi.org/10.1016/j.carbpol.2007.01.019>
- Zhang, J., Jiang, N., Dang, Z., Elder, T. J., & Ragauskas, A. J. (2008). Oxidation and sulfonation of cellulose. *Cellulose*, 15(3), 489–496. <http://dx.doi.org/10.1007/s10570-007-9193-1>