

Direct sulfation of cellulose fibers using a reactive deep eutectic solvent to produce highly charged cellulose nanofibers

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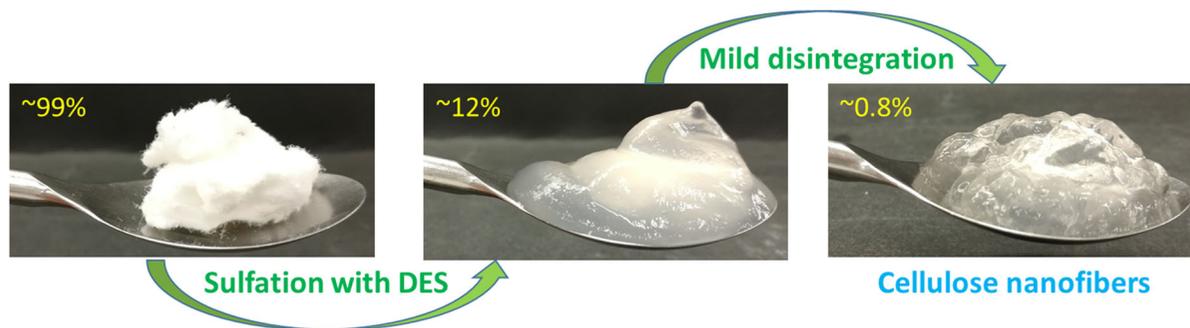
Abstract Wood cellulose pulp was sulfated using a reactive deep eutectic solvent (DES). DES was prepared by heating sulfamic acid and urea together at 80 °C at a molar ratio of 1:4, 1:3, or 1:2. Sulfation of cellulose was performed by mixing dry cellulose fibers with DES at 80 °C, followed by heating at 150 °C for half an hour. Anionic charge as high as 3 mmol/g (degree of substitution of 0.68) was obtained with this simple chemical modification of cellulose at an elevated temperature using DES both as reaction media and reagent without any external solvent. The decrease in the urea content of DES improved the sulfation efficiency. In addition, the presence of urea led to the carbamation of cellulose to some extent.

Cellulose sulfate (charge of 2.40 mmol/g) became a gel-like material in water, and after passing once through a microfluidizator, a highly transparent nanocellulose gel (transmittance of 0.1% solution at a visible light range was over 95%) was obtained. Sulfated cellulose nanofibers (SCNFs) exhibited a width of around 4 nm with a minor presence of elemental fibril aggregates (containing five or less elemental fibrils). SCNFs with high aspect ratio can have a potential end-use as a rheology modifier because of their high viscosity even at low concentrations or act as reinforcing additives.

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Graphical abstract



Keywords Cellulose · Nanofibers · Deep eutectic solvent · Sulfation

Introduction

In the field of sustainable material and chemical production, the isolation of nano-sized cellulose fibers from natural cellulose fibers has gained significant scientific and industrial interest in recent years (Charreau et al. 2013; Kim et al. 2015). Nano-sized celluloses, including long and flexible cellulose nanofibers (CNF), exhibit improved properties compared with their micro-sized counterparts, including significantly higher stiffness and strength and an enlarged surface area. The superior properties of nanocellulose can lead to the production of novel materials, such as flexible, lightweight green electronics, and even recyclable solar cells (Zhou et al. 2013, 2014). Nanocellulosic materials are also a source of biodegradable chemicals to be utilized, for example, in wastewater purification (Suopajarvi et al. 2013; Sirviö et al. 2015a; Mautner et al. 2016; Venäläinen and Hartikainen 2018).

Several methods to produce chemically unmodified nanocellulose, including pure mechanical (Turbak et al. 1983), enzymatic (Henriksson et al. 2007) and solvent based pre-treatments (Carrillo et al. 2014; Sirviö et al. 2015c; Li et al. 2017), have been introduced. However, the chemical modification of natural cellulose fibers prior to the liberation of CNFs can improve the quality of nanocellulose (e.g. more homogeneous size distribution) and lead to upgraded properties, such as ion exchange capability. In addition, the chemical pre-treatment can significantly

decrease the energy consumption of nanocellulose production (Klemm et al. 2011). Most often these pre-treatments are based on the introduction of carboxylic acid groups into cellulose by carboxymethylation (Wågberg et al. 2008; Naderi et al. 2014) or by using (2,2,6,6-tetramethyl-piperidin-1-yl)oxyl (TEMPO) (Saito et al. 2006; Fukuzumi et al. 2009) or sequential periodate-chloride oxidations (Liimatainen et al. 2012; Tejado et al. 2012).

The sulfonation or sulfation reactions have previously been used mainly for production of cellulose nanocrystals (CNC) by sulfuric acid hydrolysis (Habibi et al. 2010). The obvious drawback of sulfonated and sulfated celluloses is their poor thermal stability which limits their use, for example, in nanocomposite production (Camarero Espinosa et al. 2013). However, there are emerging fields of applications for nanocelluloses where high thermal stability is not a requirement. For example, sulfonated nanocellulose has been investigated as a sustainable water purification agent for the removal of toxic heavy metals (Suopajarvi et al. 2015), and the efficient interaction between heavy metals and sulfonated nanocellulose is obtained due to the soft–soft interaction between ligand and metals. In addition, sulfonate or sulfate groups containing nanocellulose have potential good pH-stability, e.g. in the presence of hard multivalent ligands, such as alkaline earth metal cations (Naderi et al. 2017). Good solution stability enables the more versatile uses of sulfonated nanocellulose, for example, as a thickening agent, compared with its carboxylated counterparts.

Sulfuric acid is a cheap chemical to produce nanocellulose with sulfate groups. However, due to the highly acidic condition, use of sulfuric acid leads to a hydrolysis of amorphous region of cellulose and

therefore formation of CNCs (Rånby et al. 1949) [or completely hydrolysis to sugar, depending on reaction conditions (Kim et al. 2001)]. Although CNCs have many notable properties, such as high strength, they have lower viscosity and aspect ratio compared to fibrous CNFs (Moberg et al. 2017). In addition, due to the low sulfate content, post-treatment might be requested for use of CNCs in many applications such as water purification (Batmaz et al. 2014). A significant amount of sulfuric acid (9 kg per 1 kg of CNCs) is also required, creating a significant amount of salt waste as sulfuric acid is disposed by neutralization (Chen et al. 2016). Previously, CNFs with sulfonate groups have been produced using sodium vinylsulfonate (Naderi et al. 2017). This method requests the use 2-propanol as an external solvent. In addition, post-sulfonation of CNFs has also been conducted using hazardous chlorosulfonic acid (Luo et al. 2018). In case of post-sulfonation, anhydrous condition were used together with dimethylformamide as a solvent.

The solvents are one of the main source of chemical pollution and waste during chemical and material synthesis (Clarke et al. 2018). Although they work as a heat sink and provide the even reaction conditions, traditional molecular solvents are typically volatile, flammable, toxic, or other way harmful. Novel solvent systems such as ionic liquids have been proposed as environmental friendly alternative for traditional solvents. Deep eutectic solvents (DESs) are ionic liquid analogies (sometimes classified as a sub-class of ionic liquids) and are recognized as a potential replacement for traditional molecular solvents (Smith et al. 2014). Similar to ionic liquids, DESs have a low vapor pressure, exhibit good solvent potential, and are in the best case recyclable (Jeong et al. 2015). DESs have been studied as solvents (Gutiérrez et al. 2010; Zdanowicz et al. 2016), reagents (Azizi and Alipour 2015), and catalysts (Wang et al. 2015) in organic synthesis and biomass treatment. Recently, a number of studies have emerged in which DESs are used as a solvent for cellulose derivatization (Abbott et al. 2005, 2006; Park et al. 2013; Willberg-Keyriläinen et al. 2017) and for the production of various types of nanocelluloses (Sirviö et al. 2015c, 2016; Selkälä et al. 2016; Hosseinmardi et al. 2017; Liu et al. 2017). A reactive DES has also been demonstrated in production of a derivatized, alkaline-soluble cellulose (Sirviö and Heiskanen 2017). Use of solvent as reagent is

efficient way to minimize waste formation (Clarke et al. 2018).

In this study, a reactive DES, based on sulfamic acid and urea, was investigated as a possible sulfation agent for cellulose fibers. The reaction was performed at an elevated temperature without using any external solvent, and the reaction efficiency was monitored by determining the elemental content of sulfur and nitrogen from the product. Chemical analysis of the products was performed using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. The derivatized cellulose was further mechanically disintegrated to produce sulfated CNFs (SCNFs) and characterized using ultraviolet–visible (UV–Vis) and transmission electron microscopies (TEM). Plotting out for possible use as a rheology modifier, the viscosities of the SCNF solutions at various concentrations and with the presence of various metal ions were measured using a rheometer.

Materials and methods

Materials

Softwood dissolving cellulose pulp was obtained as dry sheets (Sirvio et al. 2011). The materials were first disintegrated in water, filtered, washed with ethanol, and dried at 60 °C for 24 h.

Urea (Borealis Biuron, Austria), sulfamic acid (Sigma-Aldrich, Germany), and ethanol (VWR, France) were used as received. Metals salts (NaCl, CaCl₂, AlCl₃, FeCl₃, FeSO₄, and CuSO₄) were obtained from Sigma-Aldrich. Polylysine and phosphotungstic acid used in TEM analysis were obtained from Sigma-Aldrich. Deionized water was used throughout the experiments.

Sulfation of cellulose

The components of DES were mixed together using a magnetic stirrer in an oil bath at 80 °C at a molar ratio (sulfamic acid:urea) of 1:4, 1:3, or 1:2 until a clear solution was obtained (at around half an hour). The magnet was removed, and the desired amount of cellulose was added (10, 6, or 3 times molar excess of sulfamic acid compared with the cellulose anhydroglucose unit) and a glass rod was used to ensure that cellulose fibers were uniformly immersed in DES.

Then, the temperature of the system was increased to 150 °C (heating speed at around 5 °C/min), and the reaction was allowed to proceed for half an hour. The reaction mixture was then removed from the oil bath and allowed to cool for 5 min. The reaction was finally terminated by the addition of excess of water, followed by filtration and washing with water until the filtrate was neutral. The product was collected and stored at 4 °C.

Elemental analysis of sulfated cellulose

The samples were dried in an oven at 60 °C overnight. The nitrogen and sulfur contents of the samples were analyzed using the PerkinElmer CHNS/O 2400 Series II elemental and LECO CS-200 carbon–sulfur analyzers, respectively. The degree of substitution (DS) was calculated using Eq. 1: (Levdansky et al. 2014).

$$DS = \frac{S \times 162.15}{3206 - (S \times 97.10)} \quad (1)$$

where S is the sulfur content, 162.15 mmol/g is the molecular weight of the anhydroglucose unit, and 97.10 mmol/g is the molecular weight of the ammonium sulfate group.

Degree of polymerization

The average degree of polymerization (DP) of original cellulose pulp, DES-treated cellulose, and nanofibrillated celluloses was evaluated from the limiting viscosity, measured in CED solution according to the ISO 5351 standard. Samples were freeze-dried prior to measurement. The limiting viscosity values were converted to DP using Eq. (2),

$$DP = \left(\frac{(1.65[\eta] - 116H)}{C} \right)^{1.111} \quad (2)$$

where $[\eta]$ is the limiting viscosity, C is the mass fraction of cellulose, and H is the mass fraction of hemicelluloses. This calculation makes a correction for the contribution of hemicelluloses to the limiting viscosity number and DP of cellulose, assuming that the average DP of hemicelluloses is 140.

Disintegration of sulfated cellulose into nanofibers

The non-dried, sulfated cellulose was diluted to a consistency of 1 wt% in deionized water, mixed for 30 min using a magnetic stirrer and then passed once at a pressure of 1000 bar through the 400 μm and 200 μm chambers of a microfluidizer (Microfluidics M-110EH-30, USA) to disintegrate cellulose sulfate to SCNF.

Diffuse reflectance infrared Fourier transform spectroscopy

The chemical characterization of pristine and sulfated cellulose was performed using DRIFT. The spectra were collected with a Bruker Vertex 80v spectrometer (USA) from freeze-dried samples. The spectra were obtained in the 600–4000 cm^{-1} range, and 40 scans were taken at a resolution of 2 cm^{-1} from each sample.

Transmission electron microscopy

The morphological features of the fabricated SCNFs were analyzed with a JEOL JEM-2200FS transmission electron microscope (Japan). Each sample was prepared by dilution with ultrapure water. A carbon-coated copper grid was then prepared by coating with polylysine. A small droplet of a 0.1% solution of polylysine was placed on top of the grid and allowed to stand for 3 min. The excess polylysine was removed from the grid by touching the droplet with one corner of a filter paper. A small droplet of the diluted SCNF sample was then placed on top of the grid, and the excess of the sample was removed by the method described above. The samples were negatively stained with uranyl acetate (2% w/v in water) by placing a droplet on top of each specimen. The excess uranyl acetate was removed as described above. The grids were dried at room temperature and analyzed at 200 kV under standard conditions. The dimensions of the SCNFs were measured using the ImageJ measuring program (1.50i).

Determination of surface charge density

The surface charge density of SCNFs was determined using the polyelectrolyte titration method with a particle charge detector (BTG Müttek PCD-03,

Germany). The CDACs were diluted with deionized water into a 0.01% solution and stirred with a magnetic stirrer at room temperature for 30 min. Then, 10 ml of well-dispersed CDAC suspension was titrated with the Polydiallyldimethylammonium chloride (PolyDADMAC) polyelectrolyte. The charge density was calculated based on the consumption of titrant.

Viscosity

Viscosity of the SCNF solution at various concentrations and in the presence of 1 mM of metal salts was measured by the TA Instruments Discovery HR-1 hybrid rheometer using cone-plate geometry (cone diameter of 40 mm and cone-plate angle of 1.999°). The samples were prepared by diluting the SCNF solution to the desired concentration and mixing for 2 h with a magnetic stirrer. The samples were then allowed to stand overnight at room temperature. All measurements were conducted at 25 °C at a shear rate of 0.1–1000 1/s.

Viscosities of DESs were measured using same instrument at temperature range of 20–80 °C. Shear rate of 100 1/s was used.

Results and discussions

Sulfamic acid is a mild sulfating agent with low toxicity and is an easy-to-handle, non-hygroscopic solid, even if it is more expensive than traditional sulfating reagents such as sulfuric acid. Additionally, according to the Material Safety Data Sheet provided by supplier (Sigma-Aldrich) LD₅₀ (orally for mouse) value of sulfuric acid and sulfamic acid are 2.140 (Sulfuric acid 339741) and 3.160 (Sulfamic acid 481505) mg/kg, respectively. Sulfamic acid is proposed to form a complex with urea, and it is utilized in the sulfating of microcrystalline cellulose with organic solvent as a reaction medium (Levdansky et al. 2014). In the current study, sulfamic acid was used as part of the reactive DES for external solvent-free cellulose sulfating. A reference reaction with pure sulfamic acid could not be performed because of the high melting point of sulfamic acid (205 °C according to the manufacturer). In addition, charring of cellulose is observed when sulfation is conducted using pure

sulfamic acid in organic media (Levdansky et al. 2014). Therefore, the presence of urea can be regarded as an important factor in the sulfation of cellulose using reactive DES.

DESs are generally obtained from ionic components (e.g., quaternary ammonium salts) as hydrogen bond donors along with various hydrogen bond acceptors (e.g., carboxylic acids, glycerol, and urea) (Smith et al. 2014). Sulfamic acid is usually expressed as H₂NSO₂(OH), but it mainly exists as a zwitterionic tautomer, H₃NSO₃ (Scheme 1a). Therefore, DES-based on sulfamic acid and urea can be regarded as an analogue to the previous reported DES based on trimethylglycine (betaine) (Cardellini et al. 2014).

The reactive DESs with three different molar ratios between sulfamic acid and urea (DES1 = 1:2, DES2 = 1:3, and DES3 = 1:4) were produced by mixing the solid components at 80 °C. All three DESs existed as clear solutions, but some crystals (most likely sulfamic acid) were presented in DES1, thus indicating that the molar ratio of 1:2 is not ideal for DES formation. However, DES1 was included in the study because it showed good reactivity during cellulose sulfation. Viscosities of DESs are presented in Fig. 1. At all molar ratios, viscosities of DESs significantly decreased when temperature was increased. For example, DES3 had viscosity of 200 Pa s at 20 °C, which was decreased to 0.18 Pa s when heated to 80 °C. It is well known that viscosities of DESs can be significantly altered at elevated temperature (Fischer and Kunz 2014). The lowest viscosity at whole temperature range was observed with DES2. Therefore, molar ratio of 1:3 between sulfamic acid and urea can be seen as the optimum, especially in application where low viscosity is requested. At room temperature, all the DESs were stiff gels, which slowly started to crystallize, indicating that DESs exhibited a super-cooling behavior (Shahbaz et al. 2016; Doherty and Acevedo 2018).

As shown in Table 1, the decrease in the urea content in DES increases the reactivity. A high amount of urea may increase the occurrence of a side reaction, such as carbamation of cellulose (Scheme 1). In addition, excess urea may suppress the reactivity of the sulfamic acid–urea complex. Furthermore, when DESs with sulfamic acid:urea molar ratios of 1:4 and 1:3 were used, the decrease in sulfamic acid compared with cellulose only had a minimal effect on the sulfate group content. In the case of DES1, charge density

Scheme 1 **a** Two tautomers of sulfamic acid showing neutral (1) and zwitterionic (2) forms, **b** reaction between sulfamic acid and cellulose, and **c** possible cellulose carbamation occurring as side-reaction

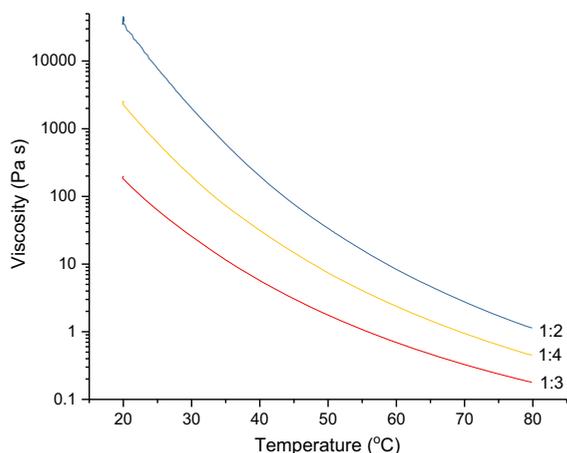
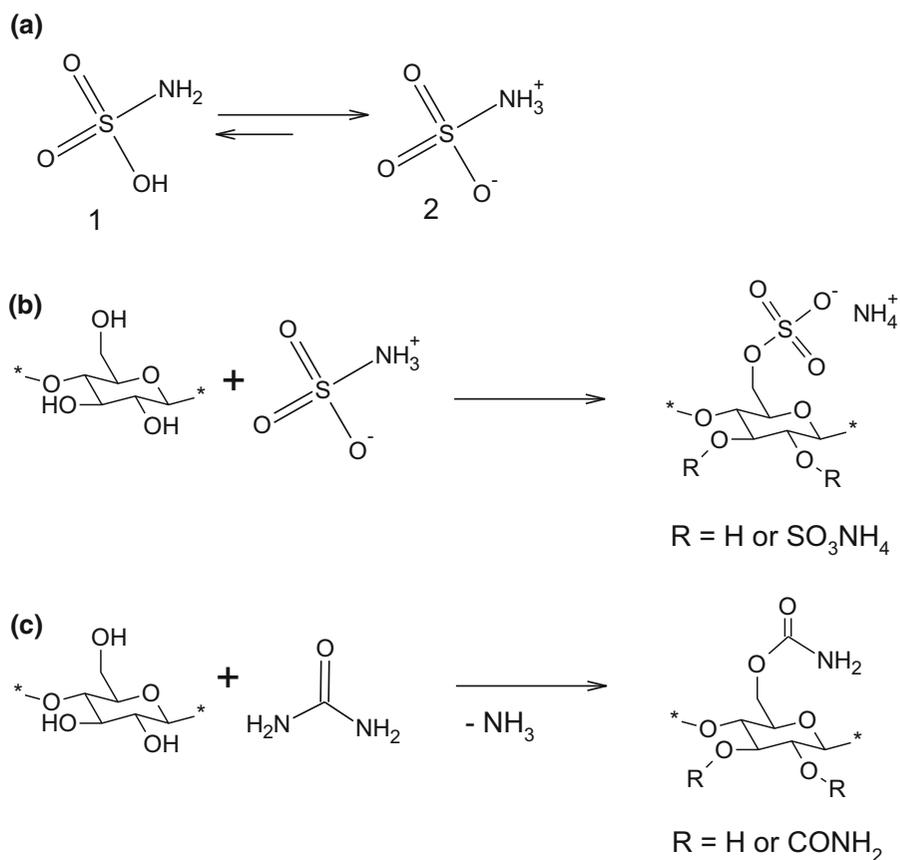


Fig. 1 Viscosities of DESs at various sulfamic acid:urea molar ratios at the function of the temperature

decreased from 3.00 to 2.40 mmol/g when the amount of sulfamic acid (relative to cellulose) decreased from 10 to 3 times the excess. The decrease in charge

density is considered modest given the fact that over three times less the amount of chemical is used.

Compared with other sulfation agent such as sulfuric acid, sulfation with sulfamic acid do not require the additional neutralization step after reaction, as the ammonium salt of sulfonic acid is produced directly after the reaction (Scheme 1b). In an ideal case, the formation of ammonium salt of sulfonic acid should also lead to an equal molar ratio between nitrogen and sulfur. In most cases, the elemental analysis of the nitrogen content showed only slightly higher values than those of the sulfur content (Table 1). However, a small excess of nitrogen compared with sulfur could indicate that some cellulose carbamation had taken place during the sulfation. Specifically, a high nitrogen–sulfur ratio was observed in Sample 7 (DES1 and 10 times the excess of sulfamic acid compared with cellulose).

During the sulfation, DP of cellulose decreased to 46–17% of original value (DP of dissolving pulp was 1822). Although a short reaction time (30 min) was

Table 1 Sulfamic acid–urea, sulfamic acid–cellulose molar ratio and cellulose content in DES reaction systems with nitrogen and sulfuric/sulfate group contents and the DS of the product

Sample	Sulfamic acid:urea molar ratio	Sulfamic acid:cellulose molar ratio	Cellulose in reaction system (w%)	S/Sulfate group content (mmol/g)	N (mmol/g)	DS*	DP**
1	1:4	10:1	4.6	1.44	1.61	0.27	854
2	1:4	6:1	7.4	1.46	1.61	0.28	712
3	1:4	3:1	13.8	1.40	1.63	0.26	452
4	1:3	10:1	5.5	1.67	1.91	0.32	545
5	1:3	6:1	8.9	1.84	2.05	0.36	741
6	1:3	3:1	16.3	1.82	2.03	0.36	499
7	1:2	10:1	6.9	3.00	4.46	0.68	848
8	1:2	6:1	11.1	2.54	2.78	0.55	747
9	1:2	3:1	19.8	2.40	2.65	0.51	310

*Calculated from the elemental content of sulfur

**DP of original dissolving pulp: 1822

utilized, the use of strong acid (sulfamic acid) containing DES and high temperature (150 °C) lead to significant hydrolysis of cellulose. Decrease in the DP of cellulose during the chemical modification, including in widely utilized TEMPO-oxidation is well known behavior (Shinoda et al. 2012). Even in the dilute acid treatment, DP of cellulose has been observed to drop significantly (Funahashi et al. 2018). In addition, previously significant decrease in the DP has been observed when cellulose treated with acidic DES (Sirviö et al. 2016). Although hydrolysis of cellulose during the chemical modification prior CNFs production can help the mechanical fibrillation and thus liberation of nanosized cellulose, it is not prerequisite, as it has been previously reported that even use of non-hydrolytic DES can help the nanofibrillation of natural fibers (Sirviö et al. 2015c; Liu et al. 2017). It should be noted that due to the significant chemical modification of cellulose with DES, the DP values calculated by limiting viscosity method should taken more as guideline than an absolute values.

Changes in the molar ratio between DES components had only minor effect of the DP of the product. Surprisingly, the reduction of molar ratio between cellulose and sulfamic acid lead to a larger decrease of DP. This can be seen as contradict to the fact that cellulose is hydrolyzed due to the presence of sulfamic acid (i.e. higher amount of sulfamic acid should lead to more severe hydrolysis). One explanation might be efficient temperature transfer during the chemical modification. As the amount of sulfamic acid

decreases, the amount of liquid in the reaction system is reduced. As the heat is not efficiently transferred from the edge of the reaction vessel, these regions might be “over heated”, resulting in more intensively hydrolysis of cellulose.

The chemical modification of cellulose was observed in the DRIFT spectra (Fig. 2). The asymmetric S=O and the symmetric C–O–S vibrations of sulfate groups were noted at around 1279 and 827 cm^{-1} , respectively (Gu et al. 2013). The C–O–S vibration was absent from the spectrum of pure sulfamic acid (Siddiqui and Ahmed 2013), thus

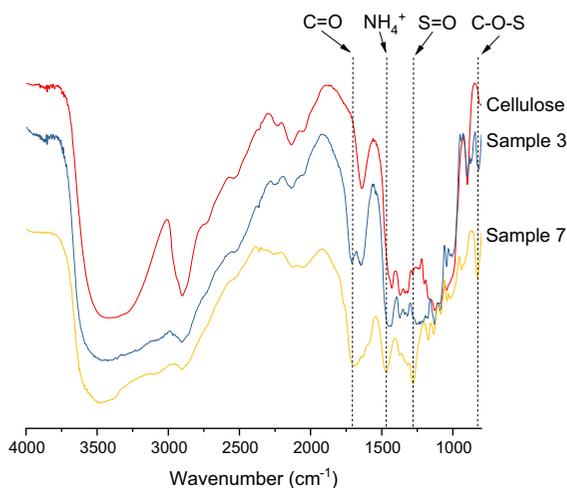


Fig. 2 DRIFT spectra of the original cellulose and two examples of sulfated celluloses; the most distinctive bands of ammonium sulfate and carbamate groups are indicated by dashed lines

indicating that the sulfate group was chemically attached to cellulose. The NH_4^+ deformation vibration was observed at 1471 cm^{-1} because of the presence of the ammonium salt of sulfate ester (Liou et al. 2011). In addition to the distinct bands of the ammonium sulfate group, the stretching vibration of the $\text{C}=\text{O}$ groups was seen at the wavenumber of 1709 cm^{-1} . The presence of carbonyl vibration (both Samples 3 and 7) confirms also the formation of the carbamate group caused by the side reaction between cellulose and urea (Yin and Shen 2007). The formation of mixed acid ester and carbamate of polysaccharide can be observed, for example, during the phosphorylation of starch in the presence of urea (Heinze et al. 2003). In addition, it has been demonstrated that cellulose carbamate can be produced using urea-containing DES (Willberg-Keyriläinen et al. 2018). Especially use of acidic betaine hydrochloride can lead to formation of cellulose carbamate with high DS.

As mentioned before, the production of sulfated (or sulfonated) nanocellulose is mainly concentrated on the production of CNCs. During CNC production, a relatively small amount of sulfate groups is attached to cellulose, and the charge group content is generally below 1 mmol/g (Bondeson et al. 2006; Abitbol et al. 2013). CNFs with a sulfonate group were previously produced using periodate oxidation followed by bisulfite addition (Liimatainen et al. 2013; Pan and Ragauskas 2014). Through sequential periodate oxidation and bisulfite addition, the sulfonate group content of $0.18\text{--}0.5\text{ mmol/g}$ was achieved. Recently, sulfoethylation was used to produce CNFs with a charge density of 0.67 mmol/g (Naderi et al. 2017). Compared with the previous results in the literature, the sulfonated samples produced here (charge densities ranging from 1.40 to 3.00 mmol/g) were potential starting materials for CNFs with a high charge density. Homogenous sulfation in ionic liquid was also used to obtain cellulose with a very high charge density (over 4 mmol/g) (Wang et al. 2010). However, aside from the need for an external solvent, this method utilizes the highly corrosive chlorosulfuric acid, which is a powerful lachrymator, and thus extreme care should be taken when handling it.

The charge densities obtained in the current study are also higher than those of highly charged carboxylated CNFs obtained by TEMPO (1.75 mmol/g) (Okita et al. 2010) and sequential periodate-chlorite (1.7 mmol/g) (Liimatainen et al. 2012) oxidations as

well as those of maleic acid esterified lignocellulose nanofibers (1.9 mmol/g) (Iwamoto and Endo 2015). However, charge density as high as 3.8 mmol/g has been obtained using esterification with succinic anhydride (Sehaqui et al. 2017). In addition, wood nanofibers with a charge density of 3.34 mmol/g has also been obtained using succinylation as pre-chemical treatment (Sirviö and Visanko 2017). High charge density is important property of CNFs, as it has been shown that a higher charge leads for example to higher removal of toxic heavy metals from wastewaters (Sehaqui et al. 2014, 2017; Sirviö et al. 2015a).

To demonstrate the potential of sulfated cellulose in nanocellulose production, SCNFs were produced from Sample 9 with DS of 0.51. Sample 9 was chosen because it was produced using the lowest amount of chemical, but its sulfate group content remained significantly high (2.40 mmol/g). In this case, the reaction efficiency, which designates the amount of reacted sulfamic acid, was 36% and the yield was 88%. The yield was calculated on the basis of the sulfate group content, but the possible presence of the carbamate group could slightly alter the calculation. Prior to mechanical disintegration, sulfated cellulose formed turbid yet stable dispersion in water (no sedimentation occurred even after several days for a 1% solution). After passing the 1% solution of sulfated cellulose only once through the microfluidizer, a transparent gel-like material was obtained (Fig. 3a). The gel-like appearance was distinct as the material could easily be dosed using a spoon after mechanical disintegration (Fig. 3b). The formation of a gel-like material is common for charged CNFs especially at a high concentrations (Naderi et al. 2014).

The UV–Vis transmittance of the 0.1% SCNF solution remained over 95% at through whole visible light spectrum ($390\text{--}700\text{ nm}$) (Fig. 3c). A high transmittance indicates that original cellulose fibers are disintegrated into even-sized nanofibers, and a negligible amount of larger unfibrillated fibers or nanofiber bundles remains. The transparency of SCNF is higher than those observed with CNF produced by TEMPO and sequential periodate-chlorite oxidations (Sirviö et al. 2014), and is close to the values obtained from the CNCs produced using sequential periodate-chlorite oxidation (Sirviö et al. 2015b). Previously, over 95% total transmittance was obtained from CNF produced from phosphorylated cellulose (0.2% solution in water) (Noguchi et al. 2017). Moreover, highly

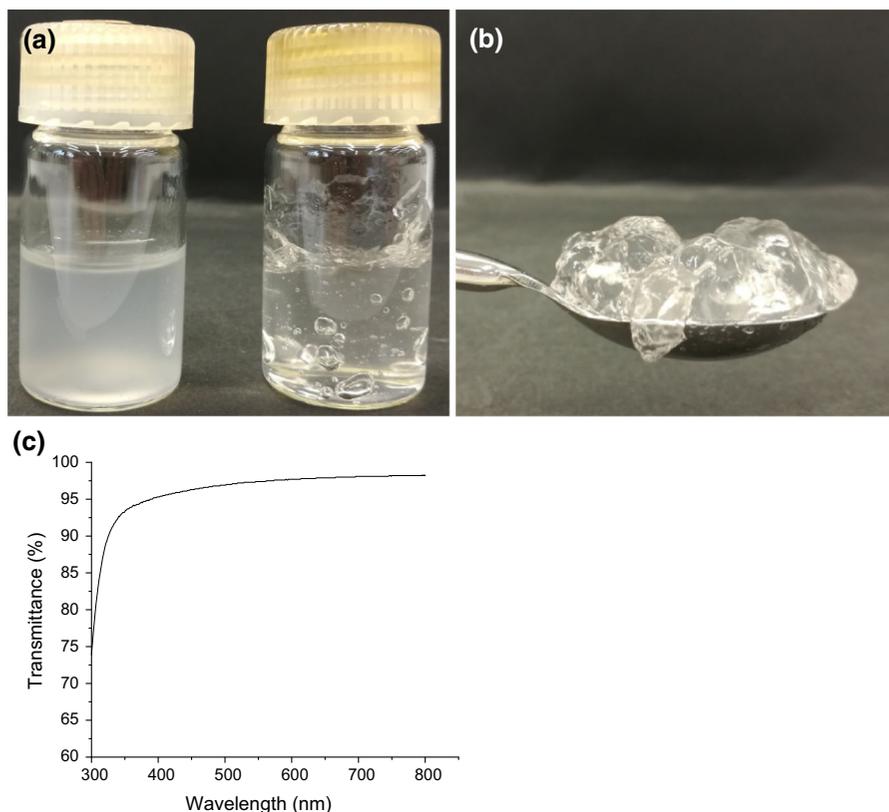


Fig. 3 **a** Sulfated cellulose (Sample 9) before and after mild fibrillation (around 1% solution), **b** demonstration of the gel-like appearance of SCNF, **c** UV–Vis spectra of sulfated cellulose (0.1% solution) after fibrillation

charged (3.8 mmol/g) succinylated CNF exhibited a transmittance of 97% at a wavelength of 600 nm (Sehaqui et al. 2017), similar to the results obtained here (98%).

Based on the TEM images, SCNF exhibited an even-sized distribution of nanofibers with an average width of $4.4 \text{ nm} \pm 1.6 \text{ nm}$ (Fig. 4). This distribution is in good agreement with the size of the elemental fibrils in wood, which is reported to have diameter of 3.5 nm (Blackwell and Kolpak 1975; Meier 2009). Some elemental fibril aggregates, with a diameter of 7–17 nm, were also presented but as minor components (see the size distribution diagram in Figure S1). The formation of even-sized nanofibrils from reactive DES sulfated cellulose fibers is most likely due to the high charge density, which creates an electrostatic repulsion between nanofibrils and enhances the penetration of water into the fiber to create osmotic pressure (Kargarzadeh et al. 2017). Both of the above-mentioned points help the formation of SCNFs even after a mild mechanical disintegration.

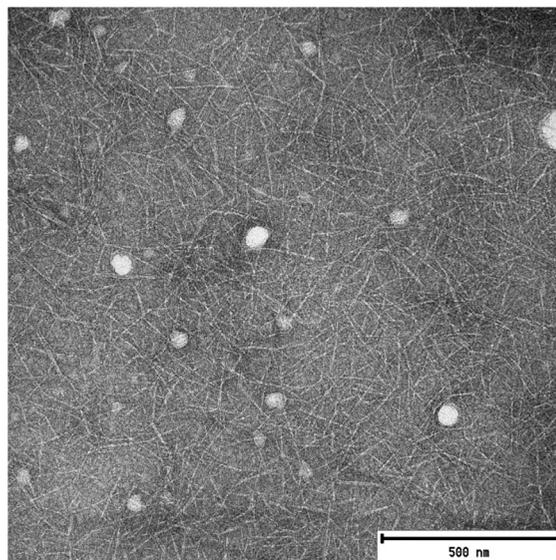


Fig. 4 TEM image of the SCNFs showing an even-sized distribution of nanofibrils

Surface charge density, measured by PE titration, of the fibrillated sample was 1.7 meq/g, demonstrating the highly anionic surface charge. Surface charge is, however, lower compared to the that predicted by elemental analysis (2.40 meq/g), which is also reported previously in literature (Liimatainen et al. 2014; Littunen et al. 2016). Due to the large polymeric structure and conformational restrictions, the titrant (polyDADMAC) used on PE titration might not have efficient interaction with significantly larger CNFs fibers having random distribution of functional groups, which might also form web-like structure even in dilute solution. Overall, PE titration still indicates that SCNFs has a high surface charge, important for example in water purification applications.

Viscosity of the SCNFs solution remained over 2500 mPa s at a shear rate below 1 s^{-1} at a concentration of 0.5–0.3% and gradually decreased when SCNFs concentration decreased (Fig. 5). At all concentrations, viscosity of the SCNF solutions decreased in the function of shear rate, indicating the typical shear thinning behavior of the CNF solution (Lasseu-guette et al. 2008). The viscosity values of the SCNFs solutions are consistent with other high-viscosity CNF solutions studied in the literature, in which viscosities over 10,000 mPa s have been reported for solutions with concentrations below 1% at a low shear rate (Pääkkö et al. 2007; Naderi et al. 2014; Moberg et al. 2017).

The SCNF solution also exhibited good stability in the presence of various metal salts (NaCl, CaCl₂,

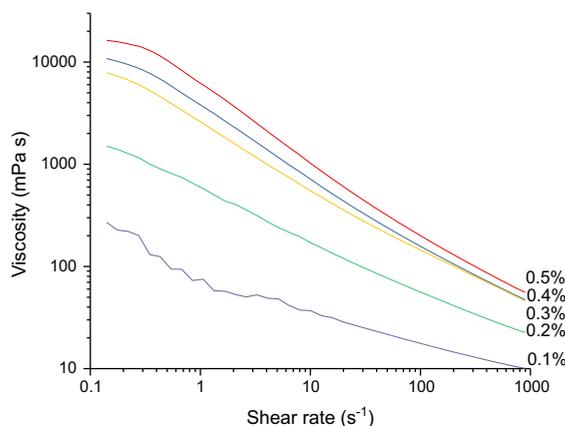


Fig. 5 Viscosities of the SCNF solutions at various concentrations (0.1, 0.2, 0.3, 0.4, and 0.5%) as a function of shear rate (0.1–1000 s^{-1})

AlCl₃, FeCl₃, FeSO₄, and CuSO₄ at a concentration of 1 mM) (Figure S2 and Table S1). The ratios between the viscosities of SCNF solutions at a concentration of 0.3% with and without the presence of metal salts were 0.6–0.8 (shear rate of 1 s^{-1}). Previously, the viscosity ratio between ethylsulfonated CNF with and without 1 mM AlCl₃ was reported to be 0.3 (Naderi et al. 2017). A direct comparison is not completely meaningful because significantly different charge densities are used. In addition, other factors, such as starting materials and solution concentration, can have a significant effect. Nevertheless, rheology measurements indicate that SCNFs can be used as a potential thickening agent for various applications. Cellulose itself inherently has low toxicity and sulfated cellulose has previously shown to have no toxicity effect (Schwartz et al. 2006; Tao et al. 2008). In addition, CNC produced using sulfuric acid hydrolysis (i.e. CNC with sulfate groups) exhibited low cytotoxicity demonstrating their potential for biomedical and biotechnological applications (Hanif et al. 2014). However, a possible toxicity effect of SCNFs should be thoroughly investigated in future studies, especially when they are to be used in food, medical, or cosmetic applications.

An additional future aspect of the utilization of reactive DES in the production of highly charged CNFs is the scaling up of the reaction. Cellulose content in reaction systems ranged from 4.6 to 19.8% (Table 1). The extended swelling of cellulose by DES caused the sulfation of cellulose to be performed without mixing, and this condition could have affected the uniformity of the reaction. In addition, viscosities of all DESs were significantly higher than many of the DESs reported in literature (Zhang et al. 2012). In addition, as stated above, low amount of solvent and absence of mixing might lead to undesired hydrolysis of cellulose. Therefore, the use of apparatus (e.g., a highly consistency reactor) may be reasonable on a large scale. Moreover, the use of powder-like cellulose, such as microcrystalline cellulose, is assumed to enable a more efficient mixing and therefore a more even reaction. On the industrial scale, one plausible method to produce sulfonated cellulose using DES is the one proposed previously for the phosphorylation of cellulose using aqueous ammonium dihydrogen phosphate (Noguchi et al. 2017). A pre-prepared dry pulp sheet is first immersed in a solvent (i.e., DES), excess solvent is removed, and the sheet is allowed to react at

the desired reaction temperature. This method can be integrated in the current paper-making facilities, but optimal sheet properties, such as thickness, should be required because they have a high impact on the even reaction between DES and fibers. Although sulfamic acid is less corrosive than traditional mineral acids such as sulfuric and hydrochloric acids (Othmer and Kirk 2007), the possible corrosive properties of DES should be investigated in future studies.

As stated above, the reaction efficiency in production of SCNFs was 36%. Previously, a reagent yield of 30% was obtained using sodium vinylsulfonate to produce sulfoethylated CNFs (Naderi et al. 2017). However, use of sodium vinylsulfonate request around 19 times excess of 2-propanol as a solvent compared to the mass of cellulose pulp. In addition, catalytic amount of NaOH was used. In case of reactive DES, only additional chemical besides the sulfamic acid (i.e. sulfating reagent) was around 2 times excess of urea compared to mass of cellulose pulp. In addition, the amount of sulfuric acid for CNC production can range from approximately 6 to 60 times excess compared to the mass of original pulp (Roman and Winter 2004). Due to the low yield [in optimized conditions yield can be as low as 30% from original mass (Bondeson et al. 2006)], the requested quantity of sulfuric acid per CNCs is very high.

When taking in the account the consumption of the chemicals during the reaction with cellulose, the amount of waste produced by the use of reactive DES per 1 g of SCNFs is approximately 1.2 g of sulfamic acid and 2.2 g of urea. The amount of waste was significantly lower compared to the salt waste produced by sulfuric acid-based production of CNC [approximately 13 g of Na_2SO_2 is produced after neutralization of used sulfuric acid (Chen et al. 2016)]. Sulfamic acid is hydrolyzed into ammonium bisulfate in water (Sulfamic acid-Ullmann's encyclopedia of industrial chemistry-metzger-Wiley online library) and if further neutralized for example into ammonium sulfate (fertilizer), amount of salt formed per one g of SCNFs is approximately 1.4 g (total waste 3.6 g). Therefore, the amount of waste produced by reactive DES is still lower compared to CNCs production. Although thoroughly comparison should be conducted (i.e. using same starting materials and similar equipment) and other factors such as energy consumption should be calculated, it can be concluded that reactive DES is potentially sustainable way to produce

nanocellulose with sulfate groups. Especially when taking into account the extremely high DS. The recycling of the chemicals would further improve the feasibility of reactive DES. Recycling might, however, request different reaction system, as sulfamic acid is hydrolyzed by water used in washing of product.

Conclusions

Reactive DES based on sulfamic acid and urea was found to be an efficient sulfating agent for cellulose fibers. A significantly high sulfate group content could be achieved using DES in external solvent-free conditions using a modest excess of sulfating chemical compared with cellulose. Sulfated cellulose could easily be disintegrated into SCNF using mild mechanical disintegration. Owing to their high viscosity even at low concentrations, SCNFs exhibit the potential to be used as a rheology modifier, for example, in hygienic or food applications. The use of easy-to-handle and environment-friendly chemicals with low toxicity and without using any external solvent makes this method a potential approach obtaining nanocellulose even on a large scale. Especially the formation of waste is significantly lower compared to the other methods, such as sulfuric acid hydrolysis of cellulose in production of CNCs.

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