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Cationization of lignocellulosic fibers with betaine in deep eutectic solvent: Facile route to charge stabilized cellulose and wood nanofibers

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ABSTRACT

In this study, a deep eutectic solvent (DES [based on triethylmethylammonium chloride (TEMA) and imidazole]) was used as a reaction medium for cationization of cellulose fibers with trimethylglycine (betaine) hydrochloride in the presence of *p*-Toluenesulfonyl (tosyl) chloride. Cellulose betaine ester with a cationic charge up to 1.95 mmol/g was obtained at mild reaction conditions (four hours at 80 °C). The reaction was further demonstrated in the fabrication of cationic cellulose nanofibers (CCNFs) by a mild mechanical disintegration of cationized cellulose. In addition to CCNFs, cationic wood nanofibers (CWNFs) were produced directly from groundwood pulp (GWP) with a high lignin content (27 w%). Individualized CCNFs and CWNFs had a fiber diameter of 4.7 ± 2.0 and 3.6 ± 1.3 nm, respectively, whereas some larger fiber aggregates (diameter below 200 nm) were also observed, especially in the case of CWNFs.

1. Introduction

Chemical modification of biomass is an important part of the biorefinery concept where natural renewable materials are utilized as sources for novel chemicals and products. Although natural biomasses have many useful properties by themselves, chemical modifications can significantly improve their feasibility in scientific and industrial applications (John & Anandjiwala, 2008; Laurichesse & Avérous, 2014; O'Connell, Birkinshaw, & O'Dwyer, 2008; Wan Ngah & Hanafiah, 2008). Using chemical modification, properties such as surface activity and solubility can be altered to meet the requirements of target applications.

Cellulose nanofibers (CNFs) are biomass-derived nanomaterials mainly obtained from delignified and bleached cellulose pulp (Kim et al., 2015; Klemm et al., 2011) and widely studied for example as reinforcement in composites (Li et al., 2018; Satyanarayana, Arizaga, & Wypych, 2009). The high energy consumption of CNF production can notably be decreased by chemical modifications. Moreover, the modifications can be used to introduce desired functionalities on the surface of nanofibers (Klemm et al., 2011). Most often these modifications are based on anionic carboxyl acid groups (Isogai, Saito, & Fukuzumi, 2011), that create electrostatic repulsion and higher osmotic pressure within fibers, which both help the liberation of CNFs during the mechanical disintegration (Lavoine, Bras, Saito, & Isogai, 2016).

In addition to anionic CNFs, cationic CNFs (CCNFs) have proven to be useful material for several applications, including flocculation (Liimatainen, Suopajärvi, Sirviö, Hormi, & Niinimäki, 2014; Suopajärvi, Sirviö, & Liimatainen, 2017a) and water purification. (Sehaqui, Larraya, Tingaut, & Zimmermann, 2015; Sehaqui et al., 2016) Cationization has been carried out using methods such as etherification with 2,3-epoxypropyl trimethyl ammonium chloride (Pei, Butchosa, Berglund, & Zhou, 2013; Sehaqui et al., 2015) and sequential periodate oxidation and imination. (Liimatainen et al., 2014; Suopajärvi et al., 2017a) These methods, however, rely on toxic and expensive chemicals. Thus, chemicals, such as natural occurring betaine, have been proposed as alternative ways for cationization of cellulose (Ma, Yan, Meng, & Zhang, 2014); but these chemicals have rarely been used in CCNFs production.

In addition to use of bleached cellulose pulp for cellulosic nanomaterial production, use of less processed natural fibers (e.g., fibers where the lignin, hemicellulose and other materials are not removed) have lately been investigated. (Hassan, Berglund, Hassan, Abou-Zeid, & Oksman, 2018; Herrera et al., 2018; Rojo et al., 2015; Visanko et al., 2017; Winter et al., 2017) For this purpose, carboxylation using (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) (Okita, Saito, & Isogai, 2009) and nitric acid or a nitric acid-sodium nitrite mixture (Sharma, Joshi, Sharma, & Hsiao, 2017) have been used. However, these methods can simultaneously solubilize non-cellulosic materials (e.g. lignin) and lead to yield losses and alteration of CNF surface characteristics. To obtain wood nanofibers (WNF) containing most of the natural lignin intact, few mechanical methods have been utilized so far. Recently, anionic WNF was produced using succinylation of groundwood pulp (GWP) in deep eutectic solvents (DES). (Sirviö & Visanko, 2017) During the succinylation, most of the original lignin (and other non-cellulosic materials) was preserved after chemical modification.

DESs are among the most promising new solvents and reagents for cellulose derivatization (Abbott, Bell, Handa, & Stoddart, 2006; Abbott,

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Bell, Handa, & Stoddart, 2005; Park, Oh, & Choi, 2013) and for production of various nanosized celluloses. (Hosseinmardi, Annamalai, Wang, Martin, & Amiralian, 2017; Li, Sirviö, Haapala, & Liimatainen, 2017; Liu et al., 2017; Selkälä, Sirviö, Lorite, & Liimatainen, 2016; Sirviö, Visanko, & Liimatainen, 2015; Suopajärvi, Sirviö, & Liimatainen, 2017b) DESs can be produced by simply mixing two or more components together, resulting in a solution having a lower melting point than any of the original components.(Smith, Abbott, & Ryder, 2014) In this work, DES, based on triethylmethylammonium chloride (TEMA) and imidazole, was investigated as reaction media for cellulose pulp cationization and production of CCNFs and CWNFs. For the reaction, trimethylglycine (betaine) hydrochloride was used as a natural-based cationization reagent, while p-Toluenesulfonyl (tosyl) chloride was accomplished as a coupling agent for the formation of an ester bond between the cellulose and betaine hydrochloride. The effect of the different reaction conditions, such as the reaction temperature and amounts of cellulose, and the betaine hydrochloride and tosyl chloride in reaction systems, were investigated. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) and elemental analysis were used for the chemical analysis of cationized materials. The production of both CCNFs and CWNFs was then demonstrated by mechanical disintegration of cationized bleached cellulose pulp and GWP. The obtained nanofibers were characterized using transmission electron microscopy (TEM).

2. Materials and methods

2.1. Materials

Unbleached spruce GWP (Visanko et al., 2017) was obtained in never-dried form, whereas the softwood dissolving cellulose pulp (Sirvio, Hyvakko, Liimatainen, Niinimaki, & Hormi, 2011) was delivered as dry sheets. The materials were first disintegrated in water, then filtered and washed with ethanol, and dried at 60 °C for 24 h.

Imidazole, TEMA, and betaine hydrochloride were purchased from TCI (Germany). Tosyl chloride and phosphotungstic acid were obtained from Sigma Aldrich (Germany) and ethanol from VWR (Finland). All the chemicals were used as obtained without purification.

2.2. Cationization of cellulose

DES was first prepared by mixing imidazole and TEMA in a beaker at a molar ratio of 2:1. The beaker was then placed in an oil bath at the desired temperature (50–100 °C) and chemicals were mixed until a clear solution was formed. Next, desired amounts of cellulose fibers were added (2–4 % according to the mass of DES), followed by the addition of betaine hydrochloride and tosyl chloride (0–4 times molar excess compared to cellulose). The reaction was allowed to proceed for four hours after which the beaker was removed from the oil bath and followed by the addition of ethanol. The product was then filtered and washed with a large amount of ethanol. The final product was dried at 60 °C for 24 h.

2.3. Elemental analysis of cationic cellulose

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) of the cationic group was calculated using Eq. (1):

$$DS = \frac{N \times 162.15}{1401-(N * 136.6)}$$

where N is nitrogen content, 162.15 the molecular weight of the anhydroglucose unit of cellulose, and 136.6 was the molecular weight of the betaine group.

Cationicity was calculated from the nitrogen content of the product (one mole of nitrogen is added by one mole of betaine group).

DS of the tosyl groups were calculated using Eq. (2):

$$DS = \frac{S \times 162.15}{3200-(S * 154.19)}$$

where S is sulfur content, 162.15 the molecular weight of the anhydroglucose unit of cellulose, and 154.19 was the molecular weight of the tosyl group.

2.4. Production of cationic cellulose and wood nanofibers

For the production of CCNFs and CWNFs, dissolving pulp and GWP were individually allowed to react with betaine hydrochloride in a similar manner described above (using two times molar excess of betaine hydrochloride and tosyl chloride at 70 °C for four hours). However, as a final step, the products were washed with water and stored in a non-dried state at 4 °C. The non-dried, cationized cellulose pulp or wood fibers were then diluted to a consistency of 0.5 wt% in deionized water, mixed for 30 s using an Ultra-Turrax (10,000 rpm). Then passed were two times at a pressure of 1000 bar through the 400 µm and 200 µm chambers and two times at 1500 bar through the 400 µm and 100 µm chambers of a microfluidizer (Microfluidics M-110EH-30, USA) to produce CCNFs and CWNFs.

2.5. Diffuse reflectance infrared Fourier transform spectroscopy

The chemical characterization of pristine and cationized cellulose and wood fibers 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.

2.6. Transmission electron microscopy

The morphological features of the fabricated CCNFs and CWNFs were analyzed with the Tecnai G2 Spirit TEM system (FEI Europe, Eindhoven, The Netherlands). Each sample was prepared by dilution with ultrapure water. A small droplet of the diluted CCNFs or CWNFs sample was placed on top of a carbon-coated and glow-discharge-treated copper grid. Then the excess of the sample was removed by touching the droplet with one corner of a filter paper. The samples were negatively stained with phosphotungstic acid (2% w/v at pH 7.3) by placing a droplet on top of each specimen. The excess phosphotungstic acid was removed as described above. The grids were dried at room temperature and analyzed at 100 kV under standard conditions. The dimensions of the CCNFs and CWNFs were measured using the ImageJ measuring program (1.50i).

2.7. X-ray diffraction

The crystalline structure of the original and cationized dissolving pulp and GWP was investigated using wide-angle X-ray diffraction (WAXD). Measurements were conducted on a Rigaku SmartLab 9 kW rotating anode diffractometer (Japan) using a Co Kα radiation (40 kV, 135 mA) (λ = 1.79030 nm). Samples were prepared by pressing tablets of freeze-dried celluloses to a thickness of 1 mm. Scans were taken over a 2θ (Bragg angle) range from 5°–50° at a scanning speed of 10°/s, using a step of 0.5°. The degree of crystallinity in terms of the CrI was calculated from the peak intensity of the main crystalline plane (200) diffraction (I_{200}) at 26.2° and from the peak intensity at 22.0° associated with the amorphous fraction of cellulose (I_{am}), according to Eq. (1) (Segal, Creely, Martin, & Conrad, 1959):

$$CrI = \left(\frac{I_{200}-I_{am}}{I_{200}}\right) \bullet 100\% \quad (1)$$