



# Fabrication of cationic cellulosic nanofibrils through aqueous quaternization pretreatment and their use in colloid aggregation



Henrikki Liimatainen<sup>a,\*</sup>, Terhi Suopajarvi<sup>a</sup>, Juho Sirvio<sup>a</sup>, Osmo Hormi<sup>b</sup>, Jouko Niinimäki<sup>a</sup>

<sup>a</sup> Fibre and Particle Engineering Laboratory, P.O. Box 4300, FI-90014, University of Oulu, Finland

<sup>b</sup> Department of Chemistry, P.O. Box 3000, FI-90014, University of Oulu, Finland

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## ABSTRACT

The aqueous pre-treatment of cellulose with periodate and Girard' reagent T was employed as a novel and promising method to promote nanofibrillation of wood pulp and to obtain cellulosic nanofibrils with cationic functionality (CNFC). To demonstrate the feasibility of CNFCs in particle aggregation, a kaolin clay model suspension was aggregated by the CNFCs. Direct high-pressure homogenization of cationized cellulose resulted in nanofibrils exhibiting typical widths of 10–50 nm and cationic charge densities ranging from 1.10 to 2.13 mequiv. g<sup>-1</sup>. The nanofibril suspensions existed in the form of highly transparent gels and possessed cellulose I crystalline structures. All of the CNFCs promoted strong aggregation of kaolin and produced voluminous kaolin-CNFC aggregates with lateral dimensions of several millimeters. Moreover, the CNFCs maintained good aggregation performance through wide pH (3–9) and temperature (25–60 °C) ranges. Thus, CNFCs were shown to be highly potential candidates for replacement of present synthetic soluble flocculation and coagulation aids.

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## 1. Introduction

Cellulose nanofibrils are nano-sized (Jarvis, 2003) elementary constituents of the cell wall of plant fibers which have been extensively investigated as promising raw materials for several high-end applications such as nanocomposites (Ho, Zimmermann, Ohr, & Caseri, 2012) self-standing films (Sehaqui, Zhou, Ikkala, & Berglund, 2011) and functional aerogels (Aulin, Netrval, Wågberg, & Lindström, 2010). In addition to their high strength and modulus (Chakraborty, Sain, & Kortschot, 2006), the nanofibrils possess a large specific surface area, a high aspect ratio and a multitude of surface hydroxyl groups, which are able to interact via hydrogen bonds. Consequently, the cellulose nanofibrils are especially promising candidates for materials in which the adhesion and interactions among the components are crucial for the materials' performances (Ho, Zimmermann, Hauert, & Caseri, 2011). However, due to anionic surface groups originating from the compounds of plant cell wall and cellulose pulp processing (Sjöström, 1989), the interaction and compatibility among anionic nanofibrils and several matrices and inorganic minerals, which are commonly negatively charged, are often poor. Moreover, the chemical pretreatments such as carboxymethylation (Wågberg et al., 2008),

TEMPO (Saito, Nishiyama, Putaux, Vignon, & Isogai, 2006) and periodate-chlorite oxidation (Liimatainen, Visanko, Sirvio, Hormi, & Niinimäki, 2012), which are used to enhance the nanofibrillation of cellulosic fibers, further increase the anionic charge density of nanofibrils. Thus, the chemical pretreatments that provide cationic charges on cellulose may promote nanofibrillation and increase the feasibility of the use of nanofibrils in many applications.

Previously, only a few pretreatment methods to obtain cationic nanofibrils have been reported. Recently, reactions with 2,3-epoxypropyl trimethylammonium chloride (Olszewska et al., 2011), glycidyltrimethylammonium chloride (Pei, Butchosa, Berglund, & Zhou, 2013) in water and etherification with chlorocholine in DMSO (Ho et al., 2011) were used to prepare cellulose nanofibrils with cationic functionality. The cationic nanofibrils exhibited good interactions with negatively charged layered silica minerals in composite structures (Ho et al., 2012) and demonstrated a high adsorption capacity toward anionic dye (Pei et al., 2013). The strong interaction between cationic nanofibrils and anionic mineral particles may also be beneficial in obtaining highly filler-loaded papers or to induce colloid particle aggregation for particle removal from fluids such as process waters. Accordingly, these materials may likely be used as high-performing green alternatives to synthetic flocculation agents and coagulants currently used in water treatment.

Dialdehyde cellulose (DAC) produced by a regioselective periodate oxidation reaction offers one potential route to introduce cationic functionality to cellulose (Sirviö, Honka, Liimatainen, Niinimäki, & Hormi, 2011; Sirviö, Hyvakkö, Liimatainen, Niinimäki,

\* Corresponding author. Tel.: +358 8553 2416; fax: +358 8553 2405.

E-mail addresses: [Henrikki.Liimatainen@Oulu.fi](mailto:Henrikki.Liimatainen@Oulu.fi) (H. Liimatainen), [Terhi.Suopajarvi@Oulu.fi](mailto:Terhi.Suopajarvi@Oulu.fi) (T. Suopajarvi), [Juho.Sirvio@Oulu.fi](mailto:Juho.Sirvio@Oulu.fi) (J. Sirviö), [Osmo.Hormi@Oulu.fi](mailto:Osmo.Hormi@Oulu.fi) (O. Hormi), [Jouko.Niinimaki@Oulu.fi](mailto:Jouko.Niinimaki@Oulu.fi) (J. Niinimäki).

& Hormi, 2011). Stable imine structures possessing quaternary ammonium groups can be synthesized by a reaction between DAC and hydrazides. Previously, Girard's reagent T ((2-hydrazinyl-2-oxoethyl)-trimethylazanium chloride, GT) was used to produce quaternized water-soluble DAC (Sirviö, Honka, et al., 2011). This reaction can be conducted in an environmentally friendly way in mild reaction conditions without the use of hazardous solvents. The toxic and expensive periodate used in the first step can be efficiently regenerated and recycled for further processing (Liimatainen, Sirviö, Pajari, Hormi, & Niinimäki, 2013) However, the literature contains no reports of this reaction route's being used for the production of cationic cellulose nanofibrils.

In this work, a cationization route based on consequent periodate oxidation and quaternization with Girard' reagent T was used as an efficient pretreatment to facilitate the nanofibrillation of wood cellulose pulp through high pressure homogenization and to fabricate quaternized nanofibrils with variable charge densities. Wide-angle X-ray diffractometry (WAXD), field-emission scanning electron microscopy (FESEM), polyelectrolyte titration and optical transmittance measurements were used to characterize the quaternized nanofibrils. Moreover, the interaction and aggregation performance of the quaternized nanofibrils in kaolin clay model suspension were examined using analytical centrifugation. In particular, the effects of nanofibril dosage, solution pH and temperature on colloid aggregation were investigated.

## 2. Materials and methods

### 2.1. Materials

Bleached birch (*Betula verrucosa* and *pendula*) chemical wood pulp obtained from the kraft pulping process was used as the raw material. The cellulose, xylan and glucomannan contents of the pulp were 74.8%, 23.6% and 1.1%, respectively, as determined using high-performance anion-exchange chromatography (HPAEC-PAD). The lignin (TAPPI-T Method 222 om-02) and the extractive contents (SCAN-CM 49:03 standard) of the pulp were 0.4% and 0.08%, respectively. The average (length-weighted) length and width of the pulp fibers, as determined using a Metso FiberLab image analyzer (Finland), were 0.90 mm and 19.0  $\mu\text{m}$ , respectively. The fines content, which was determined using a L&W STFI Fibermaster analyzer (Sweden), was 3.4%. The  $\zeta$ -potential in deionized water (conductivity  $< 5 \mu\text{S cm}^{-1}$ , pH 5.5) was determined to be  $-125 \text{ mV}$  using a Müttek SZP-06 device (Germany), and the degree of polymerization (DP) was 3817.

All of the chemicals used in the cationization of cellulose ( $\text{NaIO}_4$ , LiCl,  $[(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CONHNH}_2]\text{Cl}^-$  and HCl) and aldehyde content analysis ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ,  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}\cdot 2\text{H}_2\text{O}$ ) were obtained as p.a. grade from Sigma–Aldrich (Germany) and used without further purification.

For the charge density measurement by polyelectrolyte titration 0.1/1 M NaOH and HCl (Merck),  $\text{NaH}_2\text{PO}_4$  (Sigma–Aldrich),  $\text{NaNO}_2$  (Sigma–Aldrich),  $\text{NaCOO}$  (Sigma–Aldrich),  $\text{NaCH}_3\text{COO}$  (Oy FF Chemicals),  $\text{Na}_2\text{HPO}_4$  (Sigma–Aldrich),  $\text{NaHCO}_3$  (Merck), and  $\text{Na}_2\text{CO}_3$  (Sigma–Aldrich) were used to prepare buffers and were used without further purification. Sodium polyethensulfonate (PES-Na, BTG Müttek GmbH, Germany) was used as a titrant without further purification.

Kaolin clay was supplied as a dry powder (J.M. Huber, Finland), from which a water slurry (pH of 7.2) with a solids content of 40% was prepared with deionized water. The particle size as obtained from a Sedigraph ( $D_{50}$  value), and the surface area of the kaolin, as determined with the Brunauer–Emmett–Teller (BET) method, were 1.4  $\mu\text{m}$  and 12  $\text{m}^2 \text{g}^{-1}$ , respectively. The zeta potential and the electrophoretic mobility of the kaolin, measured in this suspension with

a Coulter Delsa 440 Doppler Electrophoretic Light Scatter Analyzer (USA), were  $-29.0 \text{ mV}$  and  $-2.2 \mu\text{m s}^{-1} / \text{V cm}^{-1}$ , respectively. The ionic strength and the pH of the kaolin suspension were modified using NaCl (Merck), NaOH (Merck) and HCl (J.T. Baker).

### 2.2. Quaternization of cellulose pulp

Cellulose pulp was cationized using subsequent periodate oxidation and reaction with Girard's reagent T ((2-hydrazinyl-2-oxoethyl)-trimethylazanium chloride, GT). Four samples with a variable charge density were produced. First, the pulp samples were oxidized with sodium metaperiodate by weighing 12 g of cellulose into a 2000 ml flask and adding 1200 ml of deionized water and 9.84 g of  $\text{NaIO}_4$ . The reaction vessels were covered with aluminum foil to prevent the photo-induced decomposition of periodate and the mixtures were stirred with a magnetic stirrer in a water bath at 55 °C with DAC 1, 65 °C with DAC 2 and 75 °C with DAC 3 and 4. LiCl (21.6 g) was used as an additive with a suspension of DAC 4. After 3 h, the products were filtered and washed several times with deionized water to remove iodine-containing compounds. DAC samples were further cationized with GT by weighing non-dried DAC (9 g abs) into a 1000 ml beaker containing 900 ml of deionized water and GT with a reagent/aldehyde molar ratio of 10 at a pH of 4.5. The mixtures were stirred for 72 h at 20 °C. Finally, the products were filtered and washed several times with deionized water. The products were stored in a non-dried state at 4 °C. The aldehyde contents of the oxidized celluloses were determined by an oxime reaction as reported previously (Sirviö, Hyvakkö, et al., 2011), while the number of cationic groups was calculated from the nitrogen content of the products, as determined with a Thermo Scientific FLASH 2000 Series CHNS/O Analyzer (USA). The synthesis route is presented in Scheme 1. FTIR spectra of freeze-dried samples were recorded using a Bruker FT-IR spectrometer (USA) using spectral width ranging from 4000 to 400  $\text{cm}^{-1}$  with 2  $\text{cm}^{-1}$  resolution and an accumulation of 32 scans. The samples were prepared by weighing out 2 mg of product and pressing it into a pellet with 200 mg of KBr.

### 2.3. Nanofibrillation of quaternized cellulose

500 ml of suspensions containing 0.5% (w/w) of cationized cellulose fibers at a pH of approximately 7 were nanofibrillated using a two-chamber high-pressure homogenizer (APV-2000, Denmark) with a pressure of 400–680 bar (flow rate of few  $\text{mL s}^{-1}$ ). The suspensions were passed through the homogenizer 3 times until clear gels were obtained (samples coded as CNFC 1, CNFC 2, CNFC 3 and CNFC 4).

### 2.4. Characterization of quaternized cellulose nanofibrils

Field Emission Scanning Electron Microscopy (FESEM, Zeiss ULTRA plus, Germany) images of the freeze-dried (liquid nitrogen and vacuum drying) and sputter-coated (coating with Pd using coating current of 40 mA and time of 30 s) samples filtered on a polycarbonate membrane with a pore size of 0.2  $\mu\text{m}$  were obtained. The accelerating voltage during imaging was 10 kV.

The polyelectrolyte titrations were performed using a Müttek PCD 03 particle charge detector (USA) by adding aqueous PES-Na (1 mequiv.  $\text{dm}^{-3}$ ) to the nanofibrils suspensions while monitoring the sign of the sample charge.

The crystalline structure of the cellulose after cationization and nanofibrillation was investigated using wide-angle X-ray diffraction (WAXD). Measurements were conducted using a Siemens D5000 diffractometer equipped with a  $\text{Cu K}\alpha$  radiation source ( $\lambda = 0.1542 \text{ nm}$ ). Samples were prepared by pressing tablets of freeze-dried cellulose to a thickness of 1 mm. Scans were taken

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