Carbohydrate Polymers 103 (2014) 187–192

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

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

Henrikki Liimatainen [a,*], Terhi Suopajärvi [a], Juho Sirviö [a], Osmo Hormi [b], Jouko Niinimäki [a]

[a] Fibre and Particle Engineering Laboratory, P.O. Box 4300, FI-90014, University of Oulu, Finland
[b] Department of Chemistry, P.O. Box 3000, FI-90014, University of Oulu, Finland

ARTICLE INFO

Article history:
Received 11 October 2013
Received in revised form 2 December 2013
Accepted 14 December 2013
Available online 25 December 2013

Keywords:
Dialdehyde cellulose
Girard' reagent T
Kaolin clay
Nanocellulose
Nanofibrillation

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^{-1}. 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.

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 (H. Liimatainen), Terhi.Suopajarvi@Oulu.fi (T. Suopajärvi), Juho.Sirvio@Oulu.fi (J. Sirviö), Osmo.Hormi@Oulu.fi (O. Hormi), Jouko.Niinimaki@Oulu.fi (J. Niinimäki).

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.12.042

& 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 μm, respectively. The fines content, which was determined using a L&W STFI Fibermaster analyzer (Sweden), was 3.4%. The ζ-potential in deionized water (conductivity < 5 μS cm^{-1}, pH 5.5) was determined to be −125 mV using a Mütek SZP-06 device (Germany), and the degree of polymerization (DP) was 3817.

All of the chemicals used in the cationization of cellulose ($NaIO_4$, LiCl, $[(CH_3)_3N^+CH_2CONHNH_2]Cl^-$ and HCl) and aldehyde content analysis ($NH_2OH{\cdot}HCl$, CH_3COOH and $CH_3COONa{\cdot}2H_2O$) 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), NaH_2PO_4 (Sigma–Aldrich), $NaNO_2$ (Sigma–Aldrich), NaCOO (Sigma–Aldrich), $NaCH_3COO$ (Oy FF Chemicals), Na_2HPO_4 (Sigma–Aldrich), $NaHCO_3$ (Merck), and Na_2CO_3 (Sigma–Aldrich) were used to prepare buffers and were used without further purification. Sodium polyethensulfonate (PES-Na, BTG Mütek 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 μm and 12 $m^2\ g^{-1}$, 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 mV and −2.2 μm s^{-1} / 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 $NaIO_4$. 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 cm^{-1} with 2 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

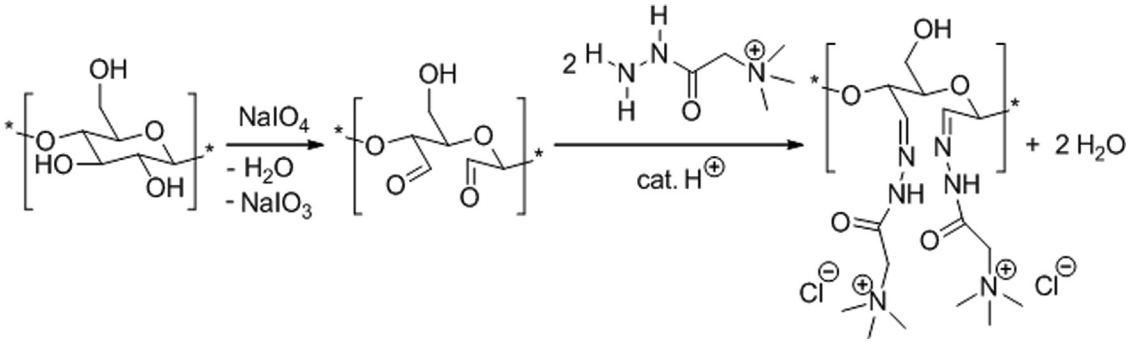
500 ml of suspensions containing 0.5% (w/w) of cationized cellulose fibers at a pH of approximately 7 were nanofibrillated using a two-chamber high-pressure homogenizer (APV-2000, Denmark) with a pressure of 400–680 bar (flow rate of few mL s^{-1}). The suspensions were passed through the homogenizer 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 μm were obtained. The accelerating voltage during imaging was 10 kV.

The polyelectrolyte titrations were performed using a Mütek PCD 03 particle charge detector (USA) by adding aqueous PES-Na (1 mequiv. 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 Cu Kα radiation source (λ = 0.1542 nm). Samples were prepared by pressing tablets of freeze-dried cellulose to a thickness of 1 mm. Scans were taken



Scheme 1. Aqueous periodate oxidation and cationization of cellulose by Girard' reagent T.

over a 2θ (Bragg angle) range from 5° to 50° at a scanning speed of 0.02° s^{-1}, using a step time of 1 s. The degree of crystallinity in terms of the crystallinity index (CrI), was calculated from the peak intensity of the main crystalline plane (0 0 2) diffraction (I_{002}) at 22.2° and from the peak intensity at 18.0° associated with the amorphous fraction of cellulose (I_{am}), according to following equation (Segal, Creely, Martin, & Conrad, 1959):

$$\mathrm{CrI} = \left(\frac{I_{002} - I_{am}}{I_{002}}\right) \times 100\% \quad (1)$$

The optical transmittance of 0.1% nanofibril suspensions was measured at wavelengths of 400–800 nm using a Hach DR 2800 spectrophotometer (USA).

2.5. Colloid aggregation of the kaolin clay suspension

The aggregation performance of the cationized nanofibrils was evaluated by aggregating a kaolin filler model suspension (solids content of 1%) and determining its residual transmission after centrifugation at 400 rpm for 300 s at 20 °C with an analytical centrifuge (LUMiFuge, L.U.M. GmbH, Germany). The centrifuge consists of a light source, a rotor above which the sample cells containing the suspension were horizontally positioned, and a CCD line sensor below the rotor. The centrifuge simultaneously measures light transmission at 800 nm over the plastic sample cells as a function of time and position. Local alterations in particle concentration and the position of the solid–liquid interface during separation are detected by changes in light transmission (von Homeyer, Krentz, Kuliche, & Lerche, 1999). Suspension aggregation is indicated by an increased sedimentation rate and reduced residual transmission.

3. Results and discussion

3.1. Preparation and characteristics of quaternized cellulose nanofibrils

Four different cationic cellulose samples with variable charge densities were prepared using consequent periodate oxidation and cationization reaction with Girard' reagent T. The charge densities (CDs) of celluloses were adjusted by modifying the reaction temperature of the periodate oxidation. The aldehyde contents of the samples after oxidations were 1.68, 2.20, 2.84 and 3.83 mmol g^{-1}, respectively, while the cationic CDs after cationization reaction were 1.10, 1.27, 1.53 and 2.25 mequiv. g^{-1}, respectively, as determined using elemental analysis. This indicated that 60–89% of aldehyde groups were converted to cationic groups, and celluloses still contained also unreacted aldehydes.

Fig. 1 shows the charge densities of quaternized samples as a function of pH, as determined using polyelectrolyte titration. The charge densities of samples were stable within the studied pH-range, and a decrease in CD of approximately 0.1 mequiv. g^{-1} was observed when the pH increased from 3 to 10, as presented in Fig. 1. Previously, a rapid decrease in the CD was observed at pH > 9 using a water soluble cellulose derivative of Girard' reagent T (Liimatainen, Sirviö, Haapala, Hormi, & Niinimäki, 2011). This phenomenon was attributed to two effects: the degradation of dialdehyde cellulose chains caused by fast β-alkoxy fragmentation that breaks the bond between carbon C-5 and oxygen O-5, and the slower auto-oxidation and peeling reactions, which continue degradations (Calvini, Conio, Lorenzoni, & Pedemonte, 2004). In this study, the degradation reaction kinetics were likely remarkably slower because the samples existed in the form of nanofibrils, which are less accessible to chemical reactions than are soluble cellulose compounds. The CDs at pH 7 obtained by polyelectrolyte titrations were substantially less than the corresponding CDs obtained from elemental analysis. This result may be observed because the fact that quaternized groups were partly inaccessible to the titrant, or because the formed titrant-cationic cellulose complexes appeared in ratios other than the stoichiometric charge ratio.

The structural characterization of quaternized celluloses was performed by the FTIR analysis (Fig. 2). Formation of an imine bond between the oxidized cellulose chain and GT was confirmed by the band at 1567.32 cm^{-1}, which is characteristic of the carbon–nitrogen double bond in imines (Lin, Yao, Chen, & Wang, 2008). The sharp bands at 1693.49 cm^{-1} and 924.81 cm^{-1} were due to the carbonyl group and the nitrogen–nitrogen bond in GT (El-Ayaan, Kenawy, & Abu El-Reash, 2007; Vojinovic et al., 2004), which coincided with the remaining aldehyde carbonyl signal and the hemiacetal band, respectively.

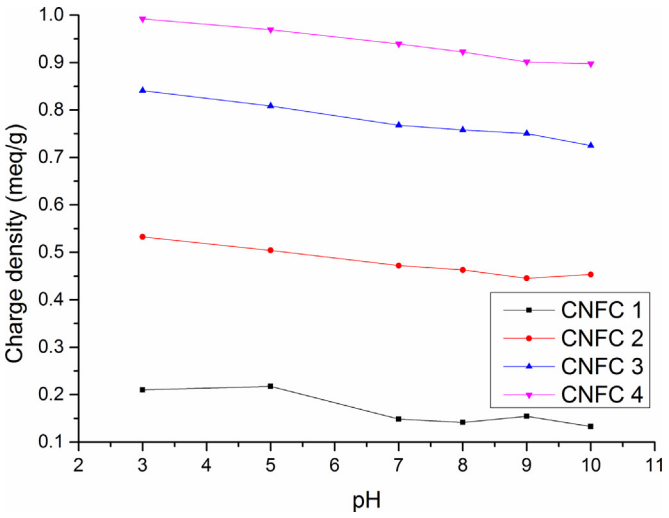


Fig. 1. Charge density of cationic cellulose nanofibrils as a function of pH.

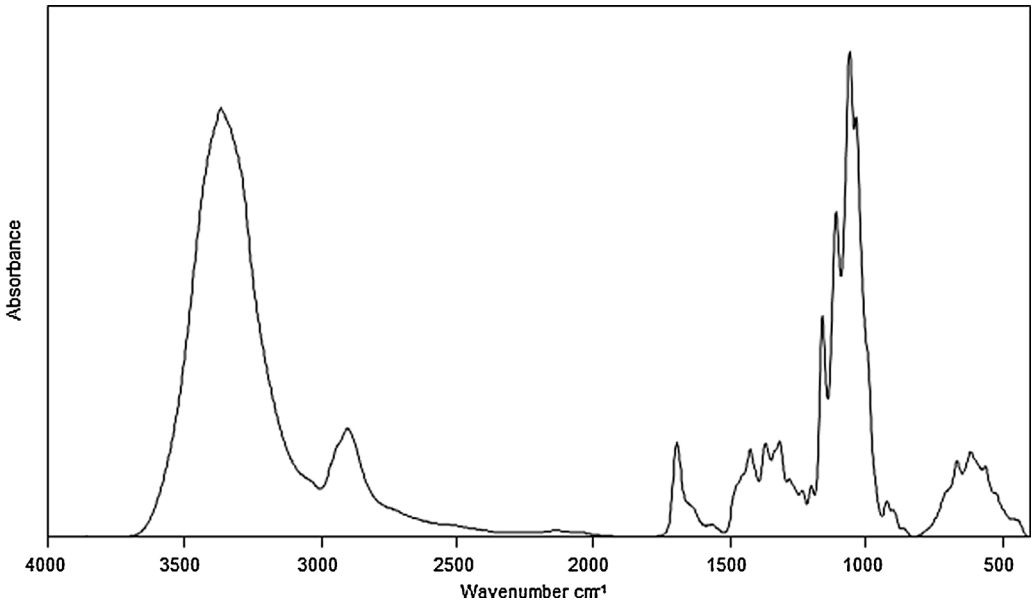


Fig. 2. FTIR spectra of cationized cellulose.

During the cationic modification, the cellulose pulp was converted to a more homogeneous and transparent form. The fibrous structure of the pulp was partly disappeared because of its increased hydrophilicity and the swelling and cutting of the cellulose. Aqueous suspensions of quaternized celluloses were further subjected to a high-pressure homogenization, in which they were easily nanofibrillated without clogging the homogenizer. After the first pass through the homogenizer, all samples existed in the form of homogeneous gels already, and after three passes, highly transparent suspensions without any visible particles were obtained. These cationic nanofibril cellulose (CNFC) suspensions were stable after long-term storage (4 weeks). No phase separation was observed, indicating that small nanofibrils with relatively high cationic charge densities were obtained.

The visual appearance of the obtained CNFC gels is presented in Fig. 3. FESEM analysis confirmed that cationic celluloses were efficiently disintegrated into nanofibrils possessing typical lateral dimensions of 10–50 nm and lengths of several micrometers (Fig. 3B). These nanofibril dimensions are comparable to cationic nanofibrils obtained earlier through a reaction with glycidyltrimethylammonium chloride (Pei et al., 2013). In addition to individual nanofibrils, the CNFC suspensions contained larger nanofibril bundles that were not completely disintegrated during homogenization.

The crystalline structure of cationic nanofibrils was investigated using WAXD. Fig. 4 shows the diffractograms of the CNFC samples (the peaks $2\theta < 10$ were associated to sample holder). Diffractogram of original pulp has been previously reported by Liimatainen, Sirviö, Sundman, et al. (2011). All cationized nanofibrils exhibited the primary 2θ diffraction angles close to 14.5°, 16.0° and 22.2°, representing peaks typical of cellulose I. These peaks are associated with the $1\,0\,1$, $1\,0\,\bar{1}$ and $0\,0\,2$ crystalline planes, respectively, and they indicate that no rearrangement of the cellulose structure into another crystalline form occurred, although the peaks broadened when the cationic charge density of the nanofibrils increased. The crystalline indeces (CrI) calculated from Eq. (1) were 38% for CNFC 1 and $30 \pm 1\%$ for all other samples (CNFC 2–4). These values indicated that the cationic modification was not fully restricted on the surface of nanofibrils, but also affected the crystalline ordering of the cellulose.

Optical transmittances for the 0.1% nanofibril suspensions in the range of 400–800 nm are shown in Fig. 5. All cationic nanofibril suspensions were highly transparent; the transmittance values were comparable or even higher than those previously reported for the individual anionic, TEMPO-oxidized cellulose nanofibrils (Besbes, Alila, & Boufi, 2011). These results support the FESEM findings, indicating that the samples contained highly fibrillated individual nanofibrils and the number of larger fibrils bundles was low.

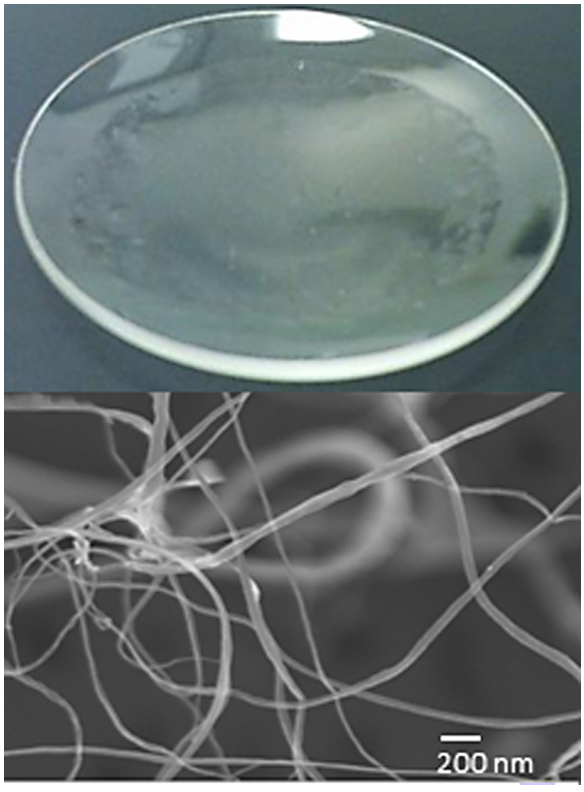


Fig. 3. (a) Appearance of 0.35% cationic cellulose nanofibrils suspension (CNFC 1) and (b) typical FESEM image of CNFC 3.

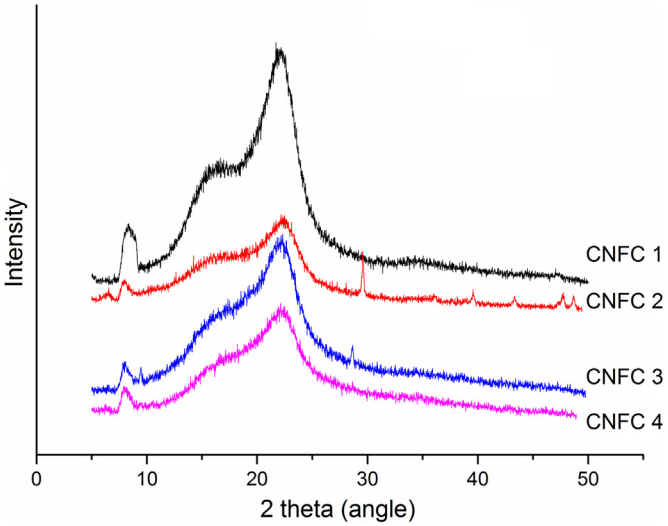


Fig. 4. WAXD diffractograms of cationic cellulose nanofibrils.

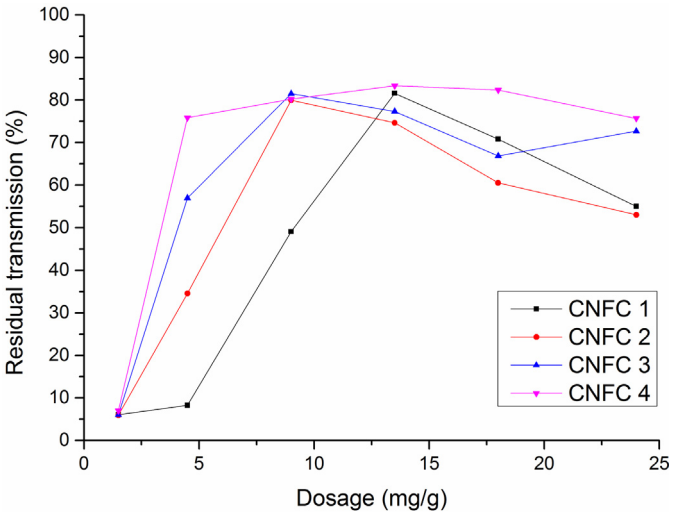


Fig. 6. Residual transmission of the clay suspension after aggregation with cationic cellulose nanofibrils and analytical centrifugation (400 rpm for 300 s at 20 °C).

3.2. Aggregation of kaolin clay colloids

Because of the high charge density and flexible, nano-sized elongated structure, CNFCs are potential candidates to replace synthetic polymeric flocculants and coagulants. In this study, the aggregation performance of the cationized nanofibrils was evaluated by aggregating a kaolin filler model suspension and determining its residual transmission after centrifugation. Fig. 6 shows the aggregation performance of CNFCs in terms of the residual transmission of the kaolin suspension as a function of CNFC dosage. All CNFC samples resulted in the clear aggregation of the kaolin clay suspension, which was indicated by the increased transmission of suspensions. Compared to previous results obtained using soluble cationic cellulose derivatives of Girard' reagent T (Liimatainen, Sirviö, Happala, et al., 2011) the transmission levels (>80%) were here remarkably higher, while the required dosages and charge densities were lower. The lowest optimum dosage among the CNFCs was achieved with CNFC 4, indicating that increasing charge density promotes the aggregation of kaolin colloids.

The visual appearance of kaolin clay aggregates obtained by optical microscopy is presented in Fig. 7. The milky appearance of the kaolin clay samples was converted to inhomogeneous and flake-like suspensions by the addition of CNFCs. The individual clay particles initially were hardly visible, but after CNFC dosing voluminous and irregular aggregates having lateral dimensions of several millimeters were detected. These aggregates were easily sedimented on the bottom of a container, forming a highly porous compactible layer.

3.2.1. Role of pH and temperature

Different solution pH values and temperatures were used to examine the aggregation performance of CNFCs in different chemical conditions. In all of these experiments, a constant polyelectrolyte dosage (13.5 mg g^{-1}) was used. The aggregation performance of CNFCs in the pH range of 3–11 is presented in Table 1. The aggregation performance maintained a constant high level from pH 3 to 9 for all samples, supporting the results of charge density measurements (Fig. 1). For the CNFC 2 and 4 samples, a slight decrease in aggregation was obtained at a pH of 10.5. This result was most likely observed because of alkaline degradation of β-alkoxy fragmentation of DAC backbone as described earlier (Calvini et al., 2004).

The aggregation performance of CNFCs was also evaluated at higher temperatures of 35–60 °C, which is a typical range for several industrial processes. The CNFCs were found to have a stable aggregation performance throughout the studied temperature range (Table 1). These results demonstrated that CNFCs are

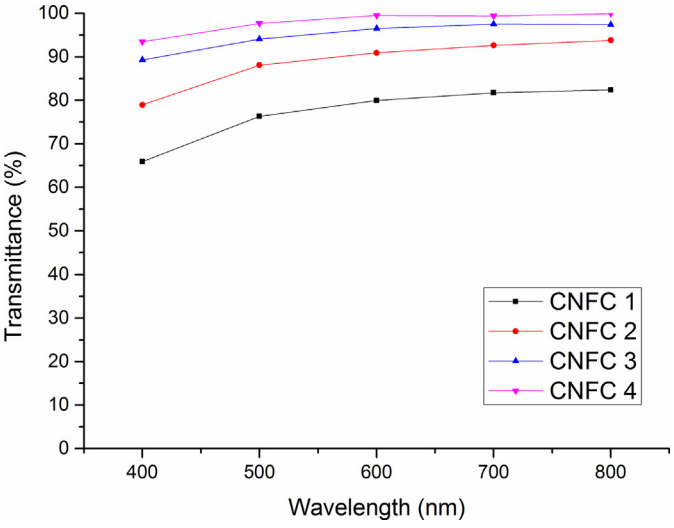


Fig. 5. Transmittance of 0.1% w/w cationic nanofibril suspensions.

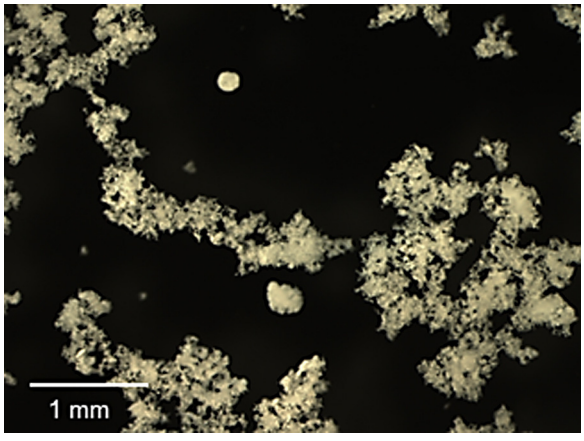


Fig. 7. Appearance of clay-cationic cellulose nanofibril aggregates.

Table 1
Influence of suspension pH and temperature on residual transmission of clay suspension aggregated by CNFC.

Variable	Residual transmission (%)			
	CNFC 1	CNFC 2	CNFC 3	CNFC 4
pH 3.0[a]	89	87	90	89
pH 4.5	87	89	90	89
pH 7.5	91	90	89	89
pH 9.0	90	90	89	89
pH 10.5	89	74	88	75
Temperature 25 °C[b]	87	90	87	90
Temperature 35 °C	88	89	88	89
Temperature 40 °C	89	90	87	87
Temperature 50 °C	89	89	87	85
Temperature 60 °C	89	89	81	74

Constant CNFC dosage of 13.5 mg g^{-1}.
[a] Temperature of 25 °C.
[b] pH of 4.5 were used.

potential candidates for several applications in which pH and temperature may vary remarkably.

3.2.2. Mechanism of clay aggregation by cationic cellulose nanofibrils

Cationic nanofibrils were found to have a natural attraction toward kaolin particles, which bore a net anionic charge in their native form. It is well-known that cationic soluble polymeric flocculants and inorganic coagulants are able to adsorb on the oppositely charged particle surfaces and to neutralize charged surface groups, which leads to particle aggregation. It is likely that cationic nanofibrils are also able to neutralize the anionic lateral surfaces of kaolin, which caused their aggregation. Enhancement of aggregation as a function of charge density of CNFC also indicates that charge neutralization is promoted as the amount of cationic charges increases (Fig. 6). The decrease in aggregation performance at higher CNFC dosages further supports this result (Fig. 6), i.e. the overdosing of cationic nanofibrils resulted in rapid charge reversal and the restabilization of kaolin particles.

4. Conclusions

Cationic cellulose nanofibrils were efficiently prepared using consequent periodate oxidation and quaternization with Girard' reagent T, in combination with high pressure homogenization. Cationic nanofibrils exhibited typical widths of 10–50 nm and charge densities ranging from 1.10 to 2.13 mequiv. g^{-1}. The nanofibril suspensions existed in a form of highly transparent gels (transmittance 80–95% at 800 nm) and possessed cellulose I crystalline structures with crystallinity indeces of 38–30%. All of the CNFCs resulted in strong aggregation of kaolin colloids and produced voluminous kaolin-CNFC aggregates with lateral dimensions of several millimeters. Moreover, the CNFCs maintained effective aggregation performance through wide pH (3–9) and temperature (25–60 °C) ranges. Thus, CNFCs were suggested as promising candidates to replace present oil-derived synthetic soluble water chemicals.

Acknowledgements

The authors acknowledge the support from the Academy of Finland and Future Biorefinery Program of Finnish Bioeconomy Cluster, FIBIC Ltd. Ms. Tuula Selkälä is gratefully acknowledged for her kind assistance in the aggregation experiments.

References

Aulin, C., Netrval, J., Wågberg, L., & Lindström, T. (2010). Aerogels from nanofibrillated cellulose with tunable oleophopicity. *Soft Matter*, *6*(14), 3298–3305.
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.
Calvini, P., Conio, G., Lorenzoni, M., & Pedemonte, E. (2004). Viscometric determination of dialdehyde content in periodate oxycellulose. *Cellulose*, *11*(3), 99–107.
Chakraborty, A., Sain, M., & Kortschot, M. (2006). Reinforcing potential of wood pulp-derived microfibres in a PVA matrix. *Holzforschung*, *60*(1), 53–58.
El-Ayaan, U., Kenawy, I. M., & Abu El-Reash, Y. G. (2007). Synthesis, thermal and spectral studies of first-row transition metal complexes with Girard-T reagent-based ligand. *Journal of Molecular Structure*, *871*(1–3), 14–23.
Ho, T. T. T., Zimmermann, T., Hauert, R., & Caseri, W. (2011). Preparation and characterization of cationic nanofibrillated cellulose from etherification and high-shear disintegration processes. *Cellulose*, *18*(6), 1391–1406.
Ho, T. T. T., Zimmermann, T., Ohr, S., & Caseri, W. R. (2012). Composites of cationic nanofibrillated cellulose and layered silicates: Water vapor barrier and mechanical properties. *ACS Applied Materials & Interfaces*, *4*(9), 4832–4840.
Jarvis, M. (2003). Cellulose stacks up. *Nature*, *426*, 611–612.
Liimatainen, H., Sirviö, J., Haapala, A., Hormi, O., & Niinimäki, J. (2011). Characterization of highly accessible microfibers generated by wet stirred media milling. *Carbohydrate Polymers*, *83*(4), 2005–2010.
Liimatainen, H., Sirviö, J., Pajari, H., Hormi, O., & Niinimäki, J. (2013). Regeneration and recycling of aqueous periodate solution in dialdehyde cellulose production. *Journal of Wood Chemistry and Technology*, *33*(4), 258–266.
Liimatainen, H., Sirviö, J., Sundman, O., Visanko, M., Hormi, O., & Niinimäki, J. (2011). Flocculation performance of a cationic biopolymer derived from a cellulosic source in mild aqueous solution. *Bioresource Technology*, *102*(20), 9626–9632.
Liimatainen, H., Visanko, M., Sirvio, J., Hormi, O., & Niinimäki, J. (2012). Enhancement of the nanofibrillation of wood pulp through sequential periodate-chlorite oxidation. *Biomacromolecules*, *13*(5), 1592–1597.
Lin, H., Yao, L. R., Chen, Y. Y., & Wang, H. (2008). Structure and properties of silk fibroin modified cotton. *Fibers and Polymers*, *9*(2), 113–120.
Olszewska, A., Eronen, P., Johansson, L.-S., Malho, J.-M., Ankerfors, M., Lindström, T., et al. (2011). The behaviour of cationic NanoFibrillar Cellulose in aqueous media. *Cellulose*, *18*(5), 1213–1226.
Pei, A., Butchosa, N., Berglund, L. A., & Zhou, Q. (2013). Surface quaternized cellulose nanofibrils with high water absorbency and adsorption capacity for anionic dyes. *Soft Matter*, *9*(6), 2047–2055.
Saito, T., Nishiyama, Y., Putaux, J. L., Vignon, M., & Isogai, A. (2006). Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose. *Biomacromolecules*, *7*(6), 1687–1691.
Segal, L., Creely, J. J., Martin, A. E., Jr., & Conrad, C. M. (1959). An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. *Textile Research Journal*, *29*(10), 786–794.
Sehaqui, H., Zhou, Q., Ikkala, O., & Berglund, L. A. (2011). Strong and tough cellulose nanopaper with high specific surface area and porosity. *Biomacromolecules*, *12*(10), 3638–3644.
Sirviö, J., Honka, A., Liimatainen, H., Niinimäki, J., & Hormi, O. (2011). Synthesis of highly cationic water-soluble cellulose derivative and its potential as novel biopolymeric flocculation agent. *Carbohydrate Polymers*, *86*(1), 266–270.
Sirviö, J., Hyvakkö, U., Liimatainen, H., Niinimäki, J., & Hormi, O. (2011). Periodate oxidation of cellulose at elevated temperatures using metal salts as cellulose activators. *Carbohydrate Polymers*, *83*(3), 1293–1297.
Sjöström, E. (1989). The origin of charge on cellulosic fibers. *Nordic Pulp and Paper Research Journal*, *4*(2), 90–93.
Vojinovic, L. S., Leovac, V. M., Novakovic, S. B., Bogdanovic, G. A., Csanadi, J. J., & Ceslje-vic, V. I. (2004). Transition metal complexes with Girard reagent-based ligands. Part I. Synthesis and crystal structure of the first cobolt(III) complexes with Schiff base derivative of Girard reagent. *Inorganic Chemistry Communications*, *7*(12), 1264–1268.
von Homeyer, A., Krentz, D.-O., Kuliche, W.-M., & Lerche, D. (1999). Optimization of the polyelectrolyte dosage for dewatering sewage sludge suspensions by means of a new centrifugation analyser with an optoelectronic sensor. *Colloid and Polymer Science*, *277*(7), 637–645.
Wågberg, L., Decher, G., Norgren, M., Lindström, T., Ankerfors, M., & Axnäs, K. (2008). The build-up of polyelectrolyte multilayers of microfibrillated cellulose and cationic polyelectrolytes. *Langmuir*, *24*(3), 784–795.