

CATIONIC AND ANIONIC NANOFIBRILLATED CELLULOSES AS DRY STRENGTH ADDITIVES FOR PAPERMAKING

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Nanofibrillated celluloses have been used in a number of applications: as thickeners, emulsifiers or additives in food, paints and coatings, cosmetics and medical devices, as reinforcing agents in composites due to their high Young modulus. Recently, papermakers have focused on their potential use for enhancing the strength properties of paper. In this study, cationic and anionic nanofibrillated celluloses were prepared by using a bleached sulphite pulp and their adsorption properties and effects on paper strength were investigated. Cationic nanofibrillated cellulose (CNFC) was produced by homogenization of pulp fibres after cationic modification with 3-chloro-2-hydroxypropyltrimethylammonium chloride. Anionic nanofibrillated cellulose (ANFC) was produced by oxidizing fibres with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), followed by final disintegration of fibres to nanofibrils by means of a high pressure homogenizer. The adsorption properties of CNFC and ANFC on silicon oxide surface were studied by means of Quartz Crystal Microbalance with Dissipation (QCM-D) in terms of adsorbed mass and viscoelastic properties. The CNFC and ANFC were also tested as additive for enhancing the dry strength of paper. Results showed that the tensile index of paper was higher when CNFC was used together with ANFC, compared with single addition of CNFC to fibre suspension.

Keywords: cationic and anionic nanofibrillated celluloses, QCM-D, paper strength

INTRODUCTION

Cellulose based materials have attracted growing attention for different purposes because cellulose is a widely abundant and sustainable material. Among these materials, nanofibrillated cellulose (NFC), which has a diameter between 5 and 100 nm and several micrometres length, has attracted researchers' attention due to its unique properties. NFC has a Young modulus of up to 135 GPa, a high strength in the range of a few GPas, as well as high aspect ratio, homogeneity, biodegradability and chemical reactivity.¹⁻³ NFC is produced by delamination of wood fibres via intense mechanical shearing forces promoted by pre-treatment with chemicals and/or enzymes. These pre-treatments contribute to increasing the inner surface and breaking cellulose hydrogen bonds and thus, enhancing fibre reactivity.^{3,4} Cellulose fibres can be disintegrated to the nanofibrillar structure by different methods, such as high pressure homogenization, microfluidization, grinding, cryocrushing and high intensity ultra-sonication.⁴ The formation of anionic groups on cellulose chain has been used

for isolation of nanofibrils. The oxidation with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) can be applied to modify C6 of glucose unit to carboxyl groups and obtain an anionic charged structure. Although, the carboxymethylation and sulfonation of glucose have been also applied, TEMPO oxidation attracts researchers because it needs very little mechanical shearing forces.⁵⁻⁷ Anionic NFC has been used in a wide range of applications, such as nanoscale papers,⁸⁻¹⁰ as papermaking additive,^{1,11} for reinforcing nanocomposites,¹²⁻¹⁷ as rheology modifier in foods, paints, cosmetics and pharmaceutical products, etc.^{3,4}

Cationic NFC (CNFC) has been investigated very rarely, compared with ANFC. The multilayers of ANFC and CNFC on SiO₂ surface, and the forces between layers have been investigated by Aulin *et al.*¹⁸ In another work, the aqueous properties of CNFC were studied and it was recorded that they depend on the pH, due to the amphoteric structure of CNFC.

The positive effect of CNFC on the water vapour barrier and mechanical properties of composites with layered silicates was remarked by Thao *et al.*¹⁹ The cationization of NFC has been conducted with different chemical treatments: 2,3-epoxypropyl trimethylammonium chloride,² glycidyl trimethylammonium chloride²⁰ and etherification with cholorocholine in DMSO.²¹ It is noteworthy that the presence of cationic groups on cellulose chains can offer advantages in a papermaking system, by replacing cationic synthetic polyelectrolytes, as well as by conferring antibacterial properties to the paper surface.^{2,22} Additionally, multi additions of cationic and anionic NFCs can also become possible for industrial application.

In this study, CNFC, produced by the pretreatment of cellulose fibres with glycidyltrimethylammonium chloride (GTMAC) and ANFC, produced by fibre oxidation with TEMPO were investigated in terms of the adsorption on silicon oxide surface and its effect on tensile index of paper. The QCM-D technique was chosen for adsorption experiments, since it has been shown to be suitable not only to determine the adsorbed amount, but also to assess the viscoelastic properties of the adsorbed layers.²⁴

EXPERIMENTAL

Materials

The bleached sulphite pulp used to produce the CNFC and ANFC was kindly supplied by Biocel Paskov a.s., Czech Republic. Bleached softwood kraft pulp (Billerund Korsnas, Karlstad, Sweden) was used to produce handsheets. TEMPO, GTMAC, NaClO₂, NaBr, NaCl, NaOH, and HCl were purchased from Sigma-Aldrich. The endoglucanase enzyme was kindly supplied by Novozymes, Denmark. De-ionised water was used in all experiments.

Methods

ANFC production

The bleached sulphite fibres were oxidized according to the method developed by Isogai *et al.*⁶ TEMPO (0.4 mmol) and NaBr (6 mmol) were added to the fibre suspension (1% concentration) in de-ionized water. After pH adjustment to 10, 2.61 g of NaClO₂ was added and the suspension was mixed mildly for 2 hours. The oxidized fibres were then washed several times until a neutral pH of the water drained from the suspension was reached. The concentration of the fibre suspension was adjusted to 0.5% and passed through APV high pressure homogenizer at 100 bar. The ANFC was stored at 4 °C until its use.

CNFC production

Cationization of fibrils was achieved according to a revised method of Aulin *et al.*¹⁸ and Zaman *et al.*²³ The sulphite pulp fibres were firstly beaten to approximately 35 °SR using a PFI mill and afterwards were enzymatically treated with 2% of endoglucanase at pH 7 using a trizma buffer at 50 °C for 2 hours. After stopping the reaction at 80 °C in an oven, the pulp was further beaten to 84 °SR and then homogenized by APV high pressure homogenizer at 500 bar 5 times resulting in a more fibrillated structure. In the cationization process, 10% of pulp fibre was put into a polyethylene bag with the addition of 1N NaOH. Then, GTMAC was added into the suspension with 4:1 ratio to anhydroglucose units in the fibres. The reaction was preceded in a water bath with ultrasonication at 65 °C for 2 hours. The suspension was kneaded by hand every 15 min during the reaction period. After cationization, fibres were precipitated with ethanol and diluted again with ethanol and precipitated via centrifugation at 4000 rpm. After washing 3 times with ethanol, fibres were washed with de-ionized water with the same procedure. The suspension of cationically modified fibre (1%) was passed through an APV high pressure homogenizer at 700 bar 10 times. The CNFC gel was stored at 4 °C until its use.

Adsorption on silicon oxide surface

The adsorption properties of polymer and complexes were studied with Quartz Crystal Microbalance with Dissipation (QCM-D, E-1 model) from Q-Sense Ab, Gothenburg, Sweden. QCM crystals coated with silica were also supplied by Q-Sense (QSX 303/50 SiO₂). With this technique, the resonant frequency of the crystal is decreased as the adsorbed mass, Δm , is increased. If the adsorbed mass is evenly distributed, rigidly attached and small compared to the mass of the crystal, then, $f - f_0 = \Delta f$ is related to the adsorbed mass per unit surface, Δm , by the Sauerbrey equation:²⁴

$$\Delta m = - \frac{C \Delta f}{n} \quad (1)$$

where n is the overtone number and C is a constant that describes the sensitivity of the device to the changes in mass for the crystals; $C = 0.177 \text{ mgm}^{-2} \text{ Hz}^{-1}$ and $n = 1, 3, 5$ or 11 .

When the driving power to the crystal is switched off, there is decay in the oscillation due to frictional losses in the crystal in the adsorbed layer and in the surrounding solution. The energy dissipation is characterized by dissipation factor D , which is related to decay time constant τ as follows:²⁵

$$D = \frac{1}{\pi f \tau} \quad (2)$$

where f is resonance frequency.

The QCM-D instrument measures the change in the dissipation factor during the adsorption process,

$$\Delta D = D - D_o \quad (3)$$

where D_o is the dissipation factor of the pure quartz crystal immersed in the solvent, D is the dissipation factor when the mass is adsorbed.

After mounting the crystal in the chamber of QCM-D, it was exposed to an aqueous buffer solution containing the same salt concentration (10^{-2} M NaCl) and pH as used for preparing the nanofibril solution to ensure a stable baseline for the frequency and energy dissipation. The adsorption experiments were then started by exchanging buffer with nanofibril solution. Residual nanofibrils were removed after 15 min by addition of the aqueous buffer solution. The Qsoft software from Q-Sense was utilized to record the changes in the properties of the adsorbed nanofibril layer at different overtones during the adsorption process. Of these, the third overtone was used for evaluation data, basically due to its stability. The concentration of the nanofibril solution was 100 mg L^{-1} in all experiments. All QCM experiments were conducted at a constant temperature of 24.0°C .

Charge density measurement

The particle charge detector PCD III (MÜTEK GmbH, Herrsching) was used to determine the charge densities of the CNFC and ANFC by the polyelectrolyte titration. The volume of the polyelectrolyte consumed to reach the isoelectric point (0 mV of streaming potential) of the samples was recorded and the charge density (q) was calculated by the following formula:²⁶

$$q = \frac{V \cdot n}{m} \quad (4)$$

where V is the volume of polyelectrolyte titrant (mL), n is titrant concentration (eq/mL), m is amount of nanofibrillated cellulose (g). Charge density was calculated in meq/g. The P-DADMAC and polyethylenesulphonate sodium salt (PES-Na) were used as standard cationic and anionic titrants, respectively.

Conductometric titration

The carboxyl content of ANFC was determined by conductometric titration. Nanofibrils (50 mg) were added to 250 mL of deionized water; after the addition of 15 mL 0.01 M HCl, the suspension was stirred for 10 minutes; ANFC suspension was then titrated with 0.01 M NaOH. The carboxyl content was calculated from the weak acid curve obtained during titration.²⁷

Imaging with Atomic Force Microscopy

The structure of the CNFC and ANFC films on SiO_2 surface was studied by means of Atomic Force Microscopy with tapping mode (Nanoscope IV, Multimode SPM, Veeco Inc., USA). All experiments using standard rectangular non-contact silicon cantilevers (RTESP, Veeco Instruments Inc., USA)

were conducted under ambient conditions (23°C and 50% relative humidity). The CNFC film was built by applying CNFC directly on the surface of SiO_2 crystal, while the ANFC was prepared on the crystal surface pre-treated with polyvinyl amine, providing cationic anchoring points for ANFC. The wet samples were then dried with N_2 gas.

Handsheet preparation and tensile strength measurement

First, the softwood kraft pulp was beaten in a PFI mill (Tappi T 248) at 40°SR ; then the pulp was diluted to 0.5% and after adjusting the pH to 7.0 ± 0.3 , CNFC was added to the suspension. After 10 min mixing at 750 rpm, 400 mL of suspension was used to obtain a handsheet on a Rapid Köthen former (Tappi T 205). Afterwards, the wet sheet was dried at 93°C at a pressure of 90 kPa for 10 min. In the experiments in which the ANFC was used, ANFC was added after the addition of CNFC at a ratio of 1:1; the suspension was mixed for 10 min after each addition. The tensile strength of the paper was measured on a Zwick Z2.5 Model Universal testing machine equipped with 2.5 kN load cell (Tappi T 494).

RESULTS AND DISCUSSION

Properties of ANFC and CNFC

The AFM images of the ANFC and CNFC films built on SiO_2 crystals are shown in Figure 1. It is clearly seen that the ANFC produced with TEMPO oxidation has a smaller size and denser layer structure than the CNFC. The selective conversion reaction of hydroxyl groups to carboxyl ones and a small amount of aldehyde groups occurs during TEMPO oxidation. The fact that the hydroxyl group of every one of two adjacent glucose units is changed to a carboxyl group has been suggested.²⁷⁻²⁹ The anionic charges of carboxyl groups cause repulsion among fibrils and result in promoted disintegration of the fibre wall. The carboxyl amount of fibrils was found as 1.6 mmol/g determined by conductometric titration. Charge density was determined as 0.9 meq/g by polyelectrolyte titration. Although aldehyde groups can also be formed by oxidation, their amount was not determined in the present study. Considering the study of Isogai *et al.*,⁶ in which the experimental conditions of oxidation were the same as in our study, the amount of aldehyde groups can be estimated less than 0.15 mmol/g.

The width and length of CNFC are larger than those of ANFC, as seen on AFM images in Figure 1. Positively charged quaternary ammonium groups were introduced to the hydroxyl groups of cellulose on the fibril surface with modification of

GTMAC.¹⁹ Even though nanofibrils have cationic charge, they also have anionic charges mainly from carboxyl groups, which are from pulping and/or bleaching processes.³⁰ The reason for the larger sizes of CNFC can be attributed to the repulsion forces among fibrils since the cationic charges are not enough to assist fibre disintegration. The charge density of CNFC was determined as 0.67 meq/g. However, it was recorded that nanocrystal cellulose modified by GTMAC reached 2.0 meq/g, depending on the concentration of the reaction mixture.²³ This charge density was achieved at a suspension concentration of 20-30%, called as semi-dry modification. In our study, there were critical points regarding when cationization should be done: before or after the homogenization process. A charge density of 0.56 meq/g was found if modification was conducted before homogenization, and a value of 0.67 meq/g when it was modified after slight homogenization. The higher surface area and thus more available

hydroxyl groups on the fibrils are possible reasons for this increase. Further studies will be done to increase the cationic charges on nanofibrillated cellulose. Smaller size can also be provided after reaching higher charge density.

Adsorption on silicon oxide surface

Adsorption properties of nanofibrillated celluloses are important for many applications, especially for the papermaking and packaging industries, where specific barrier properties are needed. QCM-D studies showed that frequency decreased significantly (-40 Hz at 3rd overtone) due to the CNFC adsorption to the negatively charged SiO₂ surface. Electrostatic interaction between CNFC and the surface was dominating the interaction for this adsorption. During rinsing of the surface with water (10⁻² M NaCl) at pH 7, the frequency increased slightly. It can be due to removing surrounding and entangled nanofibrils from the adsorbed layer of CNFC.

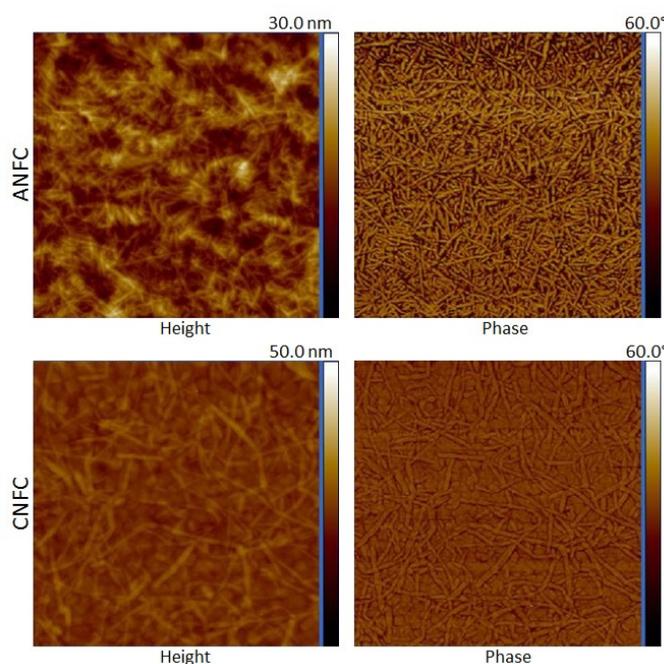


Figure 1: AFM images of ANFC and CNFC (1 μm x 1 μm)

Dissipation curves provide important data about layer structure. It is obviously seen from Figure 2 that the dissipation value increased substantially with the adsorption. A higher change due to adsorption indicates the CNFC forms a thicker and more viscoelastic layer and uptakes more water molecules. On the other hand, both

frequency and dissipation change due to the ANFC adsorption to the cationic layer of CNFC are not higher compared with CNFC adsorption to SiO₂ surface. This indicates that less adsorption of ANFC occurred, resulting in a thinner and stiffer layer because of the higher charge density and smaller size of ANFC. It is noteworthy that

dissipation decreased after ANFC adsorption. This was due to the decreasing layer thickness and/or crosslinking the CNFC layer by ANFC entering the gaps of the layer.

The amount of the mass adsorbed on the SiO_2 surface was calculated by Sauerbrey equation and the data are given in Figure 3. It is clearly seen that the adsorbed amount is about $1.2 \mu\text{g}/\text{cm}^2$, as shown in Figure 3. The adsorption is similar with that of cationic polyacrylamide (0.5 meq/g charge density and $4.6 \cdot 10^6 \text{ Da}$ molecular mass) on SiO_2 surface.³¹ After rinsing,

$0.3 \mu\text{g}/\text{cm}^2$ of mass was removed from the surface. The adsorbed amount of ANFC on CNFC layer is approximately $0.3 \mu\text{g}/\text{cm}^2$.

Dry strength of paper

The nanofibrillated celluloses with cationic and anionic charges were also used to enhance the dry strength of paper. CNFC was added to the fibre solution alone because it has an electrostatic affinity to pulp fibres, which present electronegative charge due to the carboxyl groups of pulp fibres.

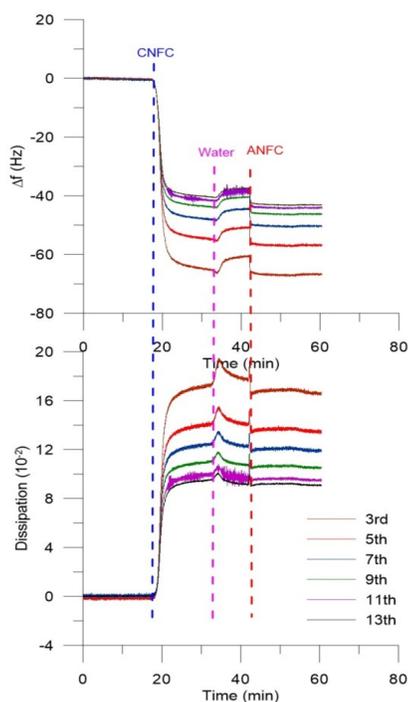


Figure 2: QCM-D data obtained during adsorption of nanofibrils (concentration 0.1 g/l , pH 7 and NaCl concentration 10^{-2} M)

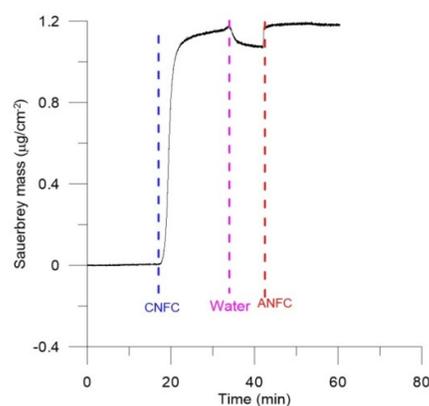


Figure 3: Adsorbed amount of nanofibrils on SiO_2 surface calculated by Sauerbrey equation

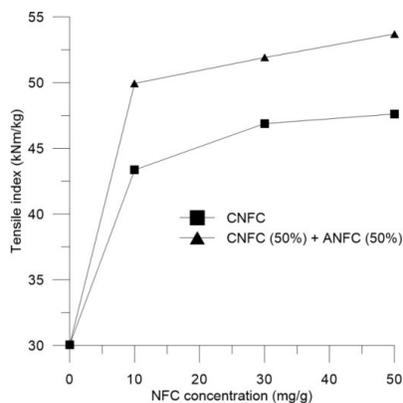


Figure 4: The effect of nanofibrillated celluloses on paper tensile index

On the other hand, the ANFC was added to the fibre suspension after treating the fibres with CNFC, giving a cationic charge on the surface for anchoring ANFC. The tensile index of paper increased from 30 kNm/kg to 47 kNm/kg by adding 50 mg/g of CNFC. However, when CNFC was used together with ANFC in a proportion of half and half, the tensile index increased up to 53 kNm/kg. The second layer with ANFC increased the molecular contact area, providing more joint points between fibres. The 3D network formation of CNFC and ANFC layers also helps interlocking and inter-diffusion mechanisms of fibrils on pulp fibres ensured by beating.

CONCLUSION

The cationic and anionic charged nanofibrils (CNFC and ANFC) were prepared using bleached sulphite pulp. As noticed from the AFM images, the CNFC produced by GTMAC modification has larger size than the ANFC produced by TEMPO oxidation. The charged groups of the CNFC do not reach the same level as those of the ANFC in promoting the disintegration of fibers to nanofibrils. Therefore, the repulsion forces between nanofibril segments can be assumed not to be high enough. Because the pulp fibres have inherently anionic charges, the formation of a slightly amphoteric structure after cationic modification can decrease repulsion forces and thus, further disintegration of fibrils is prevented. It was found from QCM-D data that CNFC forms a thicker layer than ANFC because CNFC has larger size and lower charge density. The tensile index of paper obtained by sequential addition of the CNFC and ANFC is higher compared with single addition of the CNFC to the fibre suspension. The main reason for this is the increase in the molecular contact area in the network of pulp fibres with the increasing amount of adsorbed cellulose nanofibrils. Moreover, interdiffusion of nanofibrils throughout the adjacent fibres can also increase after ANFC addition and this interlocks the fibre network more strongly, resulting in enhanced paper strength.

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