TEMPO/NaBr/NaClO-Mediated Surface Oxidation of Nanocrystalline Cellulose and Its Microparticulate Retention System with Cationic Polyacrylamide

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TEMPO/NaBr/NaClO-mediated surface oxidation of NCC, acid-extracted from aspen kraft pulp, was studied, and the properties of nanocellulose whiskers before and after oxidation were characterized by conductimetry, Fourier transform infrared spectroscopy, X-ray diffraction, and atomic force microscopy. The resulting products with varied oxidation degrees were then applied in the deinked pulp to evaluate the improvements of fines retention and pulp drainage. It was found that TEMPO-oxidized NCC maintained its crystalline form of cellulose I, while it showed better dispersibility and smaller dimension due to the high level of carboxyl content and degree of oxidation. By adding NCC and TONCC to the deinked pulp, the retention was improved while the drainage rate was decreased to some extent. When TONCC samples were applied together with cationic polyacrylamide to constitute a microparticulate retention system, both fines retention and pulp drainage were apparently improved. Further study showed that the retention and drainage rate were significantly influenced by the degree of oxidation. TONCC sample with the highest DO (0.134) gave the highest retention and drainage rate, 89.6% and 9.41 mL/s, respectively.

Keywords: Nanocrystalline cellulose; Surface oxidation; TEMPO/NaBr/NaClO; Deinked pulp; Microparticulate retention system

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INTRODUCTION

During the papermaking process, drainage and retention properties of pulps are very important parameters because they are directly related to the production efficiency of a paper machine (Allen and Lapointe 2005). Therefore, retention aids are usually needed for improving the retention and drainage abilities of pulps to increase the machine speed and paper output during the papermaking practices (Main and Simonson 1999). Although a wide variety of retention aids is now commercially available, the current papermaking relies particularly on the microparticle retention aid systems (Yan and Deng 2000), which provides a higher fine material retention, an improved formation, a higher drainage rate, and a better performance in a paper machine with high closure degree of the white water system (Hubbe 2005). Most of the microparticle applications in the papermaking industry combine a cationic polymer with an anionic microparticle (Ovenden *et al.* 2000). The cationic polymer is added to the pulp slurries in the first stage, resulting in large-scale flocculation which can be broken down by shear forces.

Then, an anionic microparticle (bentonite or colloidal silica) is added to the suspension to reflocculate the dispersed flocs through bridge formation or charge neutralization. The key parameters for forming flocculation in the microparticulate systems include the polymer charge density, the shape and surface chemistry of the microparticles, as well as the mode of microparticle interaction (Simola 2009). Microparticles with a high aspect ratio may have higher retention efficiency due to their higher bridging ability (Andersson and Lindgren 1996). Highly aggregated structured silica with high charge density gives higher fines retention with a linear chain cationic polyacrylamide (Main and Simonson 1999). Compared to montmorillonite, micropolymers with a three dimensional solid-like structure, and flexible polymer strands, tails, and loops of anionic charges provide better retention and drainage when it collaborated with cationic high mass acrylamide copolymer (Honig *et al.* 1993).

It is necessary to develop bio-based papermaking chemicals for sustainable development of pulp and papermaking industry (Shen *et al.* 2011). Many efforts have been directed at developing new chemicals from renewable resources to replace traditional oil-based products. How to effectively utilize renewable lignocellulosic resources to produce bio-based chemicals and materials is attracting the interest of scientific and industrial sectors globally (Bodin *et al*. 2006; Luo *et al*. 2012).

As an environmentally-friendly material prepared from renewable natural resources, nanocrystalline cellulose (NCC) has been receiving extended attention in the past decade (Eichhorn *et al*. 2010; Habibi, *et al*. 2010; Lima and Borsali 2004; Mihranyan *et al*. 2012). NCC has mechanical properties comparable to those of other reinforcement materials, such as carbon, high carbon steel wire, *etc.* (Hamad 2006; Wang *et al*. 2012). These features are favorable for the use of NCC in composites. It was reported that the rod-like cellulose particles acquired from different sources through acid hydrolysis have a diameter from 5 to 20 nm and a length from 100 nm to several micrometers (Beck-Candanedo *et al*. 2005; Lima and Borsali 2004). The high aspect ratio, nanometer width, and negatively charge nature may impart NCC a high bridging ability, thus constituting a microparticulate system with a cationic polymer. In our previous study (Xu *et al*. 2013), NCC was prepared from bleached aspen kraft pulp through acid hydrolysis and then applied as an additive in the deinked pulp. The results showed that the retention of fines fraction and strength properties of the pulp were both improved by applying nanocrystalline cellulose together with cationic polyacrylamide or cationic starch to constitute microparticle retention systems. However, the retention and drainage were not comparable to the conventional cationic polyacrylamide/colloidal silica or cationic starch/colloidal silica systems, which may be due to the relatively low charge density of NCC.

Ample hydroxyl groups (2 to 3 mmol g^{-1}) on the NCC surface make it possible to introduce functional groups onto the surface of NCC through heterogeneous reactions (Eyley and Thielemans 2011). Different approaches have been explored to chemically modify the NCC, such as esterification (Ifuku *et al.* 2007), oxidation (Satio *et al.* 2007), silylation (Castellano *et al*. 2004), and polymer grafting (Habibi *et al.* 2006). By chemical modifications, negative or positive electrostatic charges can be introduced onto the surface of NCC to provide it with better dispersibility and improved compatibility. In the field of chemical functionalization of NCC, a major challenge is to determine how to acquire expected surface characteristics and meanwhile avoid polymorphic conversions and maintain its crystal integrity (Habibi *et al*. 2010). The 2,26,6-tetramethyl-piperidine-1-oxyl (TEMPO)-mediated oxidation of NCC has been considered an effective approach to convert the surface hydroxyl groups to the carboxyl form for improving the dispersibility of the product (Rattaz *et al*. 2011; Habibi *et al*. 2006; Hirota *et al*. 2012; Johnson *et al*. 2009). Sulfuric acid hydrolysis of cellulose materials may charge the surface sulfate groups, thereafter providing promoted dispersibility for the resulted NCC. However, the sulfate moieties on the whiskers' surface are labile, and they can be easily removed under moderately alkaline conditions. Therefore, the stabilization is not permanent (Zaman *et al*. 2012). The TEMPO-mediated oxidation is adopted as a promising method to convert the surface hydroxyl groups into charged carboxyl entities, without the lability of sulfate groups (Habibi *et al*. 2006).

In this study, the NCC samples, extracted from the aspen kraft pulp with sulfuric acid, underwent surface modification by using TEMPO/NaBr/NaClO at pH 10. Subsequently, the surface-modified NCC samples (TONCC) were characterized by atomic force microscopy (AFM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FT-IR), and their effects on the retention and drainage of deinked pulp were examined. Furthermore, the relationships between oxidation conditions and the retention or drainage rate were evaluated and discussed accordingly.

EXPERIMENTAL

Materials

Bleached aspen kraft pulp, an original material used for preparation of the NCC samples, was provided by the Silver Star Paper Co., Ltd, Jinan, China. The 2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPO) with purity of 99% was purchased from Sigma-Aldrich Co. Ltd.

Preparation of NCC

The NCC sample was prepared according to the method by Lu and Hsieh (2012). Aspen kraft pulp was first ground with a Wiley mill, and the fraction was collected by passing through a 20-mesh screen for the hydrolysis step. Ten grams (o.d.) of the milled pulp was hydrolyzed by using 85 mL of 64 wt% sulfuric acid. Stirred for 30 min at 45 °C, the suspensions were then immediately diluted with 900 mL of deionized water to terminate the reaction. Then, the suspension was centrifuged at 3000 rpm for 15 min. The clear top layer was decanted off, and deionized water was added to mix with the thick white suspension and centrifuged again. Such a procedure was repeated 3 times. The acquired precipitate was transferred onto a cellulose dialysis membrane with a molecular weight cut-off of 12000 to 14000 Daltons and dialyzed against deionized water for 4 days until the suspension became homogeneous and the pH value became constant. The suspension were sonicated for 7 min, while cooling in an ice bath to avoid overheating. The resulting NCC was stored at 5 °C as its original wet state.

TEMPO-Mediated Oxidation of NCC

Oxidation was carried out according to the method developed by Habibi *et al*. (2006). About 1 gram of never-dried NCC solution was ultra-sonicated with a Bilon-500 Ultrasonic Sonifier for 5 min (with power of 300 W, each circulation with 1 second of ultrasonic wave, and 8 seconds of interval). TEMPO (0.1 mmol) and NaBr (6 mmol) were added into the suspension, and then a certain amount of NaClO, corresponding to 1, 2, 4, 6, and 8 mmol/g pulp, was added into the solution slowly. The pH of the mixture was maintained 10.0 to 10.5 at 25 °C by the addition of Na_2CO_3-$NaHCO_3$ buffer solution. After 60 min of reaction, the oxidation was terminated by adding 10 mL of ethanol, and the pH was adjusted to 7 by using 0.1 M HCl solution. The water insoluble fraction was recovered by centrifugation and washed thoroughly with water. The oxidized cellulose whiskers were dialyzed against distilled water with a molecular weight cut-off of 12000-14000 Daltons dialysis membrane. The acquired suspension, namely TONCC, was stored as a never-dried state at 5 °C.

X-Ray Diffraction Analysis

X-ray diffraction analyses were performed with a D8 Powder X-ray Diffractometer (Bruker AXS, Germany), which was equipped with a CuKa X-ray tube. The crystallinity was calculated according to the X-ray diffraction curve by the ratio of the crystalline area to the total area (Segal *et al*. 1959).

FT-IR

The FT-IR spectra were performed with an IRPrestige-21 Fourier Transform Infrared Spectrometer (Shimadzu Company, Japan). The samples were freeze-dried before preparing the KBr tablets. The spectra were recorded with width ranging from 400 to 4000 cm^{-1} and resolution of 2 cm^{-1}.

AFM

A Multimode 8 Nanoscope V System AFM (Bruker Corporation, Germany) was used for studying the surface characteristics of the NCC samples. A drop of sample was air dried overnight on a clean mica surface at ambient conditions for the analysis. Images from several different places on the samples were scanned.

Conductimetry

Content of carboxyl groups and degree of oxidation were determined by conductimetric titration with a DDS-11A Digital Conductivity Meter (Shanghai Hongyi Instrumentation Co. Ltd, China) (Silva Perez *et al*. 2003). A cellulose sample (50 mg) was suspended into 15 mL of 0.01 M hydrochloric acid solution. After stirring for 10 min, the suspensions were titrated against 0.01 M NaOH standard solution.

The degree of oxidation was calculated using the following formula,

$$DO = \frac{162 \times C(V_2 - V_1)}{w - 36 \times C(V_2 - V_1)} \tag{1}$$

where C is the concentration of NaOH (mol/L), w is the oven dry sample mass (mg), V_1 and V_2 are the minimum and maximum consumptions of NaOH in the conductivity (mL), respectively; the coefficient of 162 corresponds to the molecular weight of a glucose structural unit, and 36 is the difference between the molecular weight of anhydroglucose unit and that of sodium salt of a glucuronic acid moiety.

Surface Charge Density

TEMPO-mediated surface charge density of NCC samples was determined with a Streaming Current Detector (PCD03PH, Mutek Company, Germany), and polydimethyldiallylammoniumchloride (PDADMAC) was used as the standard titration reagent. The surface charge density was calculated based on the formula as follows,

$$\text{Charge density} = \frac{V \times C}{Wt} \tag{2}$$

where V is the volume consumption of the PDADMAC (mL), C is the concentration of PDADMAC (eq/g), and Wt is the sample weight (g).

Retention Ratio and Drainage Rate Measurement

A Britt Dynamic Drainage Jar (a 100-mesh screen) was used for determining retention and drainage of pulp suspensions. Pulp furnish (500 mL) containing deinked fibers, NCC, TONCC samples, and 20% of precipitated calcium carbonate (on o. d. fibers) were employed in the test.

In the monocomponent retention test, various dosages of NCC and TONCC were added into the pulp furnish under the agitation speed of 750 rpm. Thirty seconds later, the first 100 mL of filtrate was collected and the time for collection was recorded to calculate the drainage rate according to the formula as follows:

$$\text{Drainage rate}\ (\text{ml/s}) = 100/time \tag{3}$$

Light transmittance was measured at the wavelength of 500 nm using a Hitachi UV 4100 spectrophotometer (Hitachi, Japan). The concentration of filtrate was calculated according to the curve of light transmittance against filtrate concentration, and the first pass retention (FPR) of furnish was calculated according to the following formula,

$$\text{FPR}(\%) = (1 - C/C_0) \times 100\% \tag{4}$$

where C is the concentration of filtrate and C_0 is the concentration of the pulp furnish. In the dual-component retention test, the cationic polyacrylamide was added into the pulp furnish, and then stirred at the speed of 1500 rpm for 30 s. Then, the stirring speed was reduced to 750 rpm, and NCC, TONCC were added. The drainage rate and the FPR could be calculated according to Eq. 4.

RESULTS AND DISCUSSION

Charge Density and DO of Oxidized Whiskers

NCC samples, extracted from bleached aspen kraft pulp by sulfuric acid hydrolysis, were oxidized using the TEMPO/NaBr/NaClO system at pH 10 with varied amounts of NaClO. The relationships between the amount of NaClO and DO or yield are depicted in Fig. 1. It was shown that DO was significantly increased after the TEMPO oxidation, which suggested that the surface hydroxymethyl groups had already been carboxylated. This is in agreement with the results of previous studies (Habibi *et al*. 2006; Isogai *et al*. 2011). The DO was increased with the increase of NaClO, and it reached a plateau when NaClO addition was 4 mmol/g. However, the yield was decreased with the increase of NaClO. More carboxylate groups, resulted from the progressive TEMPO-oxidation, would probably make the oxidized whiskers water soluble (Hirota *et al*. 2012), which consequently decreased the yield. Generally, the higher the DO was, the lower the yield acquired.

The surface charge density of the NCC and TONCC versus pH values is shown in Fig. 2. Obviously, the surface charge density was significantly affected by the pH value of the solution. NCC demonstrated its highest charge density, 160 μeq/g, at pH of 7. After this point, the charge density tended to decrease under alkaline conditions, which resulted from the hydrolysis of sulfate moieties. The sulfate moieties at the whisker surface were labile, being easily removed under moderately alkaline conditions, which agreed with the result reported by De Nooy *et al*. (1994). For the oxidized samples, the charge density increased with the increase of pH and was more stable under the moderately alkaline conditions, because the carboxylate groups introduced onto the cellulose surface through the oxidation remained stable under the conditions. This attribute is very important to extend its application in the papermaking process, because the environment of the wet end of papermaking is usually under neutral or mild alkaline conditions. It was also shown that the charge density increased greatly after the oxidation, *i.e.*, a 10-fold increase, due to the formation of carboxylate groups on the whiskers surface.

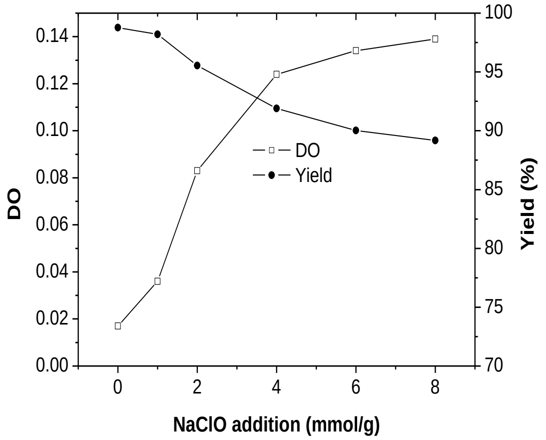


Fig. 1. Relationships between the amount of NaClO and DO or yield

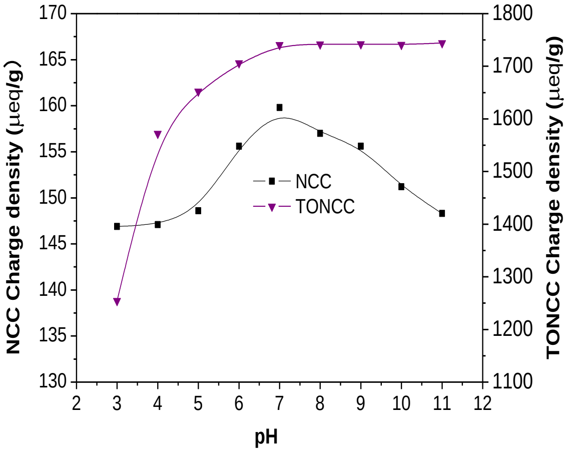


Fig. 2. Surface charge density of NCC and TONCC (oxidized with 4 mmol/g of NaClO) at various pH

Chemical Structure of Oxidized Whiskers

The TEMPO oxidation of the whiskers was detected in the FT-IR spectra, as shown in Fig. 3. The absorption bands around 1730 cm^{-1} corresponded to the stretching vibration of C=O in carboxyl groups (Habibi *et al*. 2006), however, these absorption bands were absent for the samples of aspen kraft pulp and NCC, which indicated that the carboxyl groups were introduced into the TONCC after TEMPO-mediated surface modification. The intensity of the absorption increased with the continuous addition of NaClO, which corresponded well with the increase of DO.

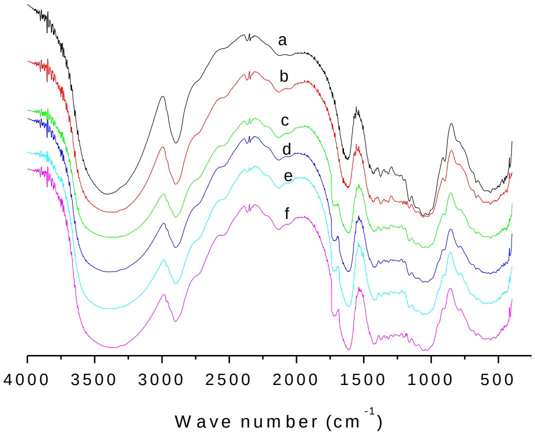


Fig. 3. FT-IR spectra of the samples: a, original aspen kraft pulp; b, NCC; c, d, e, and f, oxidized with 1, 2, 4, and 8 mmol/g of NaClO, respectively

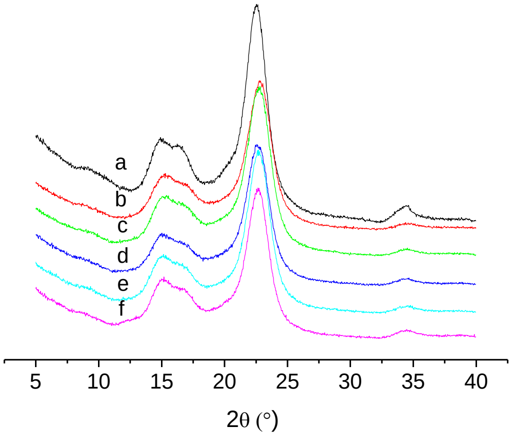


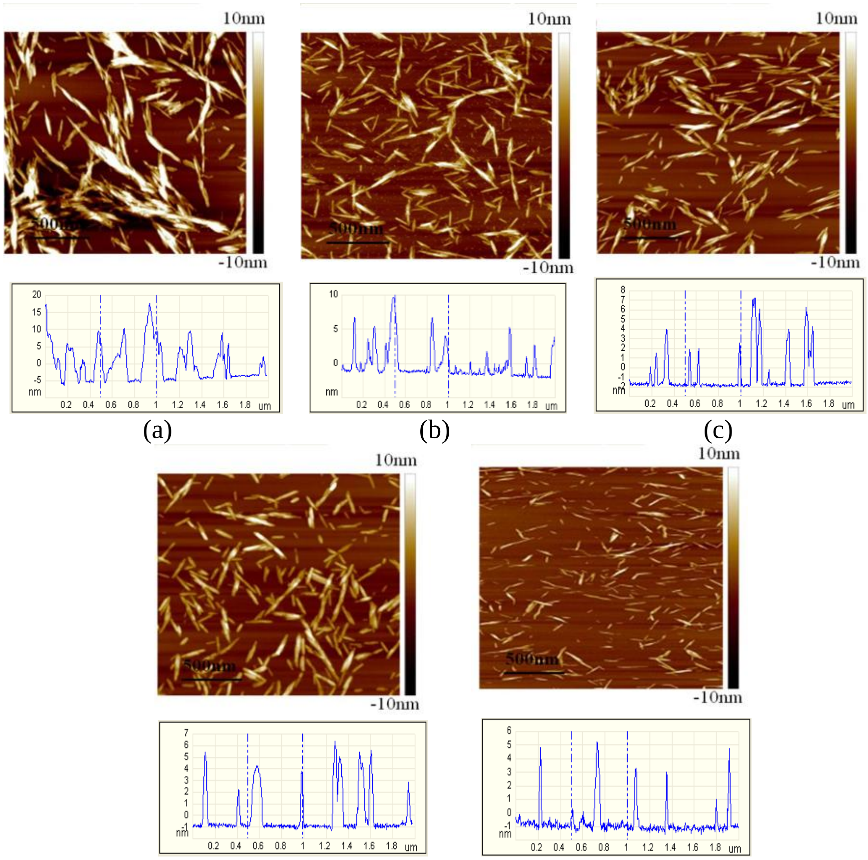
Fig. 4. Wide-angle X-ray diffraction pattern of the samples: a, original aspen kraft pulp HBKP; b, NCC; c, d, e. and f, oxidized with 1, 2, 4, and 8 mmol/g of NaClO, respectively

The wide-angle X-ray diffraction patterns of cellulose whiskers were investigated (Fig. 4). The peaks at 2θ=14~18°, 22.5°, and 34.5° were characteristic of the structure of cellulose I (Klemm *et al*. 2005). The crystal structure of cellulose I was not changed after the oxidation. Compared to the untreated kraft pulp, an apparent higher crystallinity was achieved for the NCC sample. Meanwhile, the crystallinity did not significantly change after the TEMPO oxidation, which indicates that the carboxylate groups formed during the oxidation were present only on the whiskers' surfaces without any internal cellulose crystallites. This was quite similar to the study of Johnson *et al*. (2009), who reported the

TEMPO process produces no change in crystallinity of cellulose even at a high oxidation level of 10 mmol NaClO per gram of cellulose.

Surface Morphology of Oxidized Whiskers

The NCC and TONCC samples were observed by using an atomic force microscope, and their morphologies are shown in Fig. 5.



(a) (b) (c)

(d) (e)

Fig. 5. Dimensional dynamic AFM images: a, NCC; b, c, d, and e, oxidized with 1, 2, 4, and 8 mmol/g of NaClO, respectively. Z-profile graph was taken across the image from an arbitrary horizontal line.

The image of Fig. 5a shows the typical external features of NCC prepared by acid hydrolysis, which had aggregated due to the limited electrostatic repulsion, and its morphology was quite similar to what has been reported in the literature (Jean *et al.* 2008). As expected, the dispersibility of TONCC, shown in Fig. 5b, c, d, and e, were significantly improved compared to that of the NCC. In addition, this improvement increased with the increase of NaClO addition. This was probably due to the higher carboxyl content introduced during the oxidation, which consequently increased the electrostatic repulsion between the nanoparticles.

As shown in Fig. 5, the height profile of the line along the length of the cellulose whiskers was plotted, which revealed that the width of nanowhiskers was decreased from about 10-15 nm to 5-7 nm after the oxidation. It could be observed from the images that the better dispersibility led to smaller width. The widths of TONCC particles were almost unchanged, with varied addition of NaClO, which agreed with the crystallinity results.

Retention and Drainage of Deinked Pulp in the Presence of TONCC

NCC might be considered as a potential natural retention aid due to its large specific surface area and high aspect ratio (Xu *et al*. 2013). Four samples, NCC, TONCC-1 (1 mmol/g of NaClO), TONCC-2 (2 mmol/g of NaClO), and TONCC-3 (4 mmol/g of NaClO), were used in the experiments to evaluate the influence of oxidation degree on the retention and drainage properties of the deinked pulp. As shown in Fig. 6, the FPR was increased expectedly by addition of nanocellulose whiskers. Meanwhile, the drainage rate was decreased. It is understandable that the negatively charged nanocellulose whiskers can induce a weak flocculation, which is similar to the action of anionic high molecular mass polyacrylamide (Liu *et al*. 2003), and subsequently to the benefit of the retention of fines and fillers. The strong water retention property of NCC, due to their huge surface area (up to several hundred m^2/g) and ample surface hydroxyl groups (2 to 3 mmol g^{-1}) (Eyley *et al*. 2011), deteriorates pulp drainage. The drainage result is in accordance with the report of Taipale *et al*. (2010), who studied the effect of microfibrillated fibrils on the drainage of kraft pulp. Praskalo *et al*. (2009) investigated sorption properties of TEMPO-oxidized cotton and lyocell fibers. It was found that the water retention values of the TEMPO-oxidized fibers increased with increasing NaClO charge and oxidation time, which is due to the introduction of hydrophilic carboxyl groups and morphological changes. Obviously, the hydrophilicity of TONCC samples negatively influenced the drainage property, *i.e.* the drainage rate was decreased with the increase of DO. TONCC 2 and TONCC 3 gave almost the same FPR and drainage rate, especially at addition level of more than 0.4%, probably because of the lesser difference of carboxyl-ate content between these two samples. In general, the FPR was slightly increased by the addition of NCC, while the drainage was deteriorated.

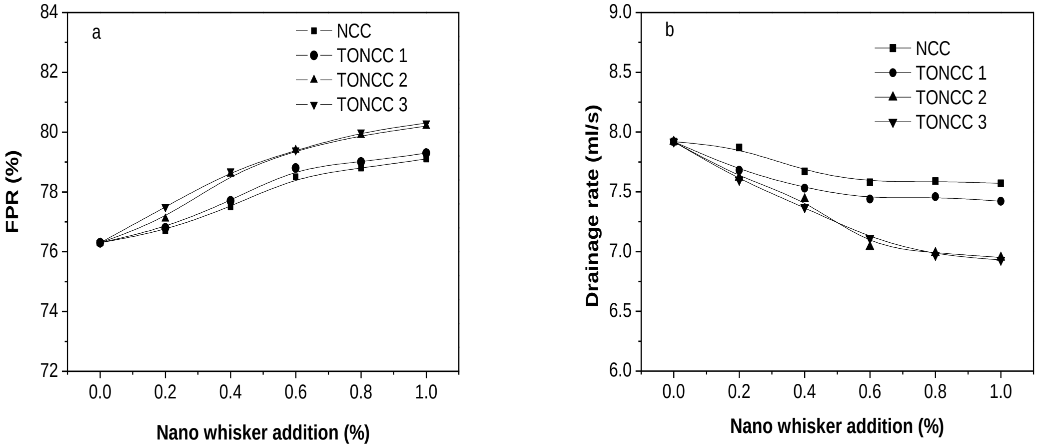


Fig. 6. Effect of addition of nanocellulose on the retention (a), and drainage rate (b) of the deinked pulp

NCC samples were then used with the deinked pulp as an anionic microparticle, together with cationic polyacrylamide (CPAM), to constitute a microparticle retention system. The results of the FPR and drainage rate are demonstrated in Fig. 7. Compared to the monocomponent system, the drainage rate, and especially the FPR, were improved for the microparticulate system. The FPR was greatly improved by adding CPAM. The addition of CPAM resulted in the primary flocculation of fiber, fines, and filler. These initial flocs were broken down by shear forces mainly through breakage of polymer chains (Hubbe *et al*. 2009). Then, nanocellulose whiskers interacted with the CPAM chains with extended conformation and induced a rapid consolidation and dewatering of the floc, resulting in smaller, denser, and stronger flocs, by which the retention and drainage were apparently improved. Previous work suggests that swollen polymers would resist the dewatering process (Hubbe 2005). After the addition of TONCC particles, due to its high negative charge density, the coils of cationic acrylamide copolymers tend to wrap around the microparticles, and the complexes formed would cause the coils of CPAM to contract and expel water. In addition, the hydroxyl groups on the whisker surface were also involved in the drainage improvement. The hydroxyl groups in nanocellulose whiskers bind water through hydrogen bonding (Ahola *et al*. 2008) and hence deteriorate the pulp drainage. Due to the trend of adsorption of anionic cellulose whiskers on the highly cationic polyacrylamide chains, the nanowhiskers have fewer opportunities to form hydrogen bonds with water, and thus, the drainage rate was further improved.

Higher effectiveness for retention might tend to hurt the formation uniformity. Andersson and Lindgren (1996) reported that by selecting a microparticle with larger size, it is possible to shift the benefits of the microparticulate system more to the retention efficiency and away from an exclusive concentration on the formation. In this study, the TONCC samples have long particle length, which could improve the retention effectiveness. However, no obvious change of apparent sheet uniformity was observed based on the visual appearance, probably due to the small, tight flocs formed by the microparticulate system. The retention and drainage properties of pulps were, to a large extent, influenced by the oxidation degree for the system with involvement of TONCC. The FPR and drainage rate increased with the increase of the DO, probably due to the increase of the electrostatic attraction forces between nanocellulosic particles and CPAM.

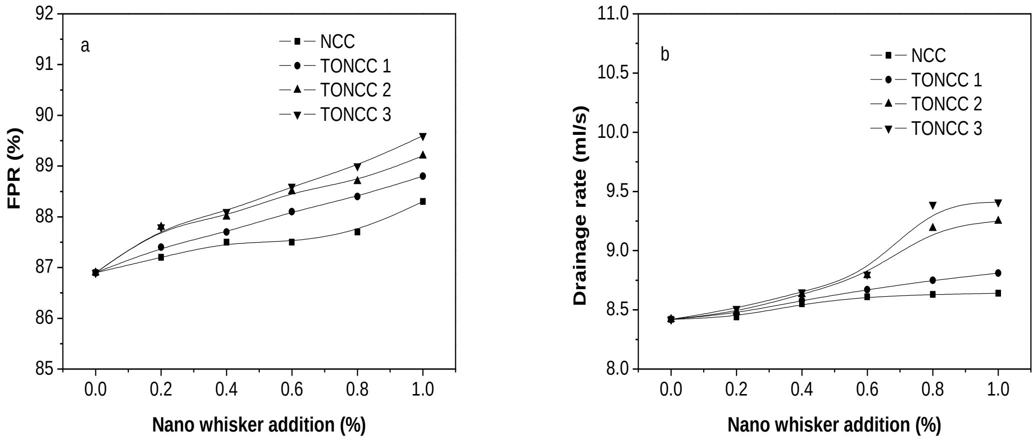


Fig. 7. Effect of nanocellulose addition on the retention (a) and drainage rate (b) of the deinked pulp applied together with CPAM as a microparticle retention system

CONCLUSIONS

1. Carboxylate groups were introduced onto the surface of NCC samples by the oxidation with TEMPO/NaBr/NaClO, and its surface charge density increased significantly. The sulfate moieties on the NCC surface were labile, and easily

removed under moderately alkaline conditions, while carboxylate groups on the surfaces of TONCC were basically kept stable.

2. After TEMPO oxidation, the crystal structure of cellulose remained in the structure of cellulose I. The dispersibility was consequently improved, and the particle width was reduced.
3. With addition of NCC and TONCC in the deinked pulp, the retention increased, while the drainage rate decreased to some extent.
4. When TONCC samples were applied together with cationic polyacrylamide to constitute a microparticulate system, both the retention and the drainage rate of the pulp were improved.
5. The oxidation degree of NCC has significant influence on the retention and drainage properties. With the increase of the DO, the FPR and drainage rate increased, which suggests that the electrostatic attraction forces between nanocellulose and CPAM play a key role in the flocculation formed by the microparticulate system.

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