Utilizing Cellulose Nanofibril as an Eco-Friendly Flocculant for Filler Flocculation in Papermaking

Ming He, Byoung-Uk Cho, Yong Kyu Lee, and Jong Myoung Won*

Cellulose nanofibril (CNF) is a type of nano-sized cellulosic material with a high aspect ratio and a large specific surface area, which makes it a promising additive to flocculate particles such as fillers. In this study, CNFs were prepared by wet disk-milling with three different degrees of fibrillation. The effect of the CNF on the flocculation of precipitated calcium carbonate (PCC) was elucidated. A photometric dispersion analyzer (PDA) investigated the flocculation phenomena resulting from the interactions between the PCC and the CNF, or polymers, in real-time. The results clearly showed that CNF could be used to control the flocculation behavior of the PCC particles. Scanning electron microscopy (SEM) images showed that the CNFs functioned as bridges between the two PCC particles. A significant reflocculation capability was observed in one- and two-component systems that consisted of CNFs. The addition of cationic starch (C-starch) could induce more efficient flocculation within a two-component system.

Keywords: Cellulose nanofibrils (CNF); Precipitated calcium carbonate filler; Flocculation; Cationic starch; Photometric dispersion analyzer (PDA)

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INTRODUCTION

Paper is a complex sheet composite consisting of cellulose-based fibers and additives such as fillers, pigments, sizing agents, and processing aids. For almost all kinds of printing and writing quality papers, the fillers are the most significant portion of these additives on a weight related basis. Fillers have been used to improve paper quality and to reduce material and energy costs. Because there is no mutual attraction between the wood fibers and fillers, small mineral particles (generally less than five microns) will pass through the forming wire and be lost from the sheet (Yoon and Deng 2006). Thus, retention aids have been added in the wet end of the papermaking process to increase the retention of these small particles, and to flocculate and bind them into a paper web. Cationic polymers, often polyacrylamides copolymers, are the most commonly used retention aids. Because of their versatile tailorability, synthetic polymers are very efficient flocculants. However, they are not biodegradable and shear resistant. The drawbacks of using these polymers include the increasing costs of petroleum feedstocks, their very slow biodegradability in soil and water, and the toxicity of their residual monomer, which is usually present in small amounts (Shogren 2009). Recently, the use of biodegradable and renewable carbohydrate polymers, such as starch, cellulose, and chitosan in filler flocculation has become a very interesting research topic (Yoon and Deng 2006; Shen *et al.* 2008; He *et al.* 2015). Because common inorganic fillers, such as clay and calcium carbonate, are not capable of forming sufficiently strong bonds with fibers, filler preflocculation with the carbohydrate polymers enhances the affinity between the fillers and fibers, endowing the fillers with certain beneficial attributes (Shen *et al.* 2010).

Cellulose is a linear, high-molecular-weight, natural polymer consisting of repeating β-(1→4)-D-glucopyranose units and is the most abundant natural polymer on Earth (Roy *et al*. 2009). Cellulose and its derivates have drawn attention in recent filler flocculation studies. Biswal and Singh (2006) studied grafted carboxymethylated cellulose as a flocculant of fillers, and Liimatainen *et al.* (2011) examined cationically modified cellulose biopolymers to induce the aggregation of fillers.

In the past decade, there has been a lot of research activity in the field of cellulose nanofibrils (CNF) and cellulose microfibrils (CMF). Generally, CNFs or CMFs can be produced by mechanical disintegration, such as refining or high-pressure homogenization (Iwamoto *et al.* 2008), cryocrushing (Chakraborty *et al.* 2005), microfluidization (Zimmermann *et al.* 2010), grinding (Yong *et al.* 2015), or high-intensity ultrasonication (Petersson and Oksman 2006). Although the chemical composition and high aspect ratio of cellulose fibrils can be preserved, the cellulose fibrils produced by mechanical disintegration are heterogeneous in size and the production may require high-energy consumption. To fibrillate fibers effectively, various pretreatment methods have been used to reduce the pulp fiber length and/or weaken the interactions between the fibrils within the cell wall such as acid hydrolysis (Henriksson *et al.* 2007), alkaline treatment (Wang and Sain 2007), enzymatic hydrolysis (Pääkko *et al.* 2007), 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation (Saito *et al.* 2006), and carboxymethylation (Wågberg *et al.* 2008). Through these methods, the properties of the fibrils, such as their size and surface charge, can be modified.

The decrease in size of fibers from micro-scale to nano-scale in width accomplished by mechanical force offers a new potential for materials with unique properties, such as high mechanical strength, large specific surface area, high aspect ratios, barrier properties, biodegradability, and biocompatibility (Eichhorn *et al.* 2010; Kwon and Shin 2016). Because of these properties, they have already shown promising results in several fields, such as medicine (Cai *et al.* 2014), rheology modification (Dimic-Misic *et al.* 2013), composite materials (Hubbe *et al.* 2008), high strength films (Henriksson *et al.* 2008), strength improvement of paper (Kajanto and Kosonen 2012), and the flocculation and retention of particles (Suopajärvi *et al.* 2013; He *et al.* 2016). Suopajärvi *et al.* (2013) reported that the anionic nanofibrillated dicarboxylated cellulose bioflocculants showed good performance in the aggregation treatment of municipal waste water. Kajanto and Kosonen (2012) found that the use of CNF as a reinforcement agent in paper could give a considerable increase in the tensile strength, enabling up to 8 g/m^2 grammage reduction. The filler retention can also be increased with CNF. In a previous study, CNF was used to flocculate fillers with C-starch (He *et al.* 2016). The results showed that the filler retention remained around 90% in handsheets, with the addition of 2% CNF. With the nature of high aspect ratio and a large specific surface area, CNF can bind and flocculate small particles, such as fines and fillers, acting as a retention aid. Jin *et al.* (2014) found that cellulose nanofiber can be applied as an anionic microparticle to constitute a microparticulate system with cationic polyacrylamide (CPAM) to flocculate the kaolin clay suspension. However, they did not report how the cellulose nanofiber affected the kinetics of flocculation. Furthermore, an excessive level of flocculation is not desired, as it leads to non-uniform paper formation. The degree of flocculation and reflocculation, which affects the floc characteristics, plays an important role on the retention and dewatering process, depending on the type of predominant flocculation mechanism (Norell *et al.* 1999; Yoon and Deng

2004). In the course of papermaking, particles may flocculate, deflocculate, or reflocculate simultaneously. There has been limited research on the flocculation of filler by CNFs. Therefore it is necessary to understand how CNF affects the kinetics of flocculation and reflocculation of filler applied in the wet end of papermaking.

The aim of this study was to elucidate the effect of CNFs on the flocculation of precipitated calcium carbonate (PCC), a widely used filler in a variety of paper grades, and find the conditions that induce an optimum PCC floc size during the papermaking process. In this paper, CNFs with different degrees of fibrillation and various polymers were used in flocculation experiments. Moreover, a two-component system in which CNF was combined with C-starch was also studied. The PCC aggregation was analyzed using particle size measurement, photometric dispersion analysis (PDA), and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

Bleached hardwood kraft pulp (Acacia, April, Indonesia) and PCC (Hankuk Paper Ltd., Korea) were used as raw materials for this study. A PCC slurry with a solids content of 15% (w/w) was used. The mean size of the PCC (scalenohedral type) was 2.2 μm, and the zeta-potential of the PCC was 4.72 mV. An anionic polyacrylamide (APAM, charge density (CD) -0.86 meq/g, molecular weight (MW) 1,000 to 1,200 × 104 g/mol), and two types of cationic polyacrylamide (CPAM) (CPAM-L: CD 0.5 meq/g, MW 150 × 104 g/mol; and CPAM-H: CD 2.0 meq/g, MW 500 to 600 × 104 g/mol) were used. The anionic polyacrylamide (APAM) and the two types of cationic polyacrylamide were obtained from SongKang Industrial Co., Ltd., Korea. The cationic starch (C-starch, CD 0.28 meq/g), which had a degree of substitution (DS) of 0.04, was supplied from SamYang Genex Corp., Korea. Before use, 2 g /L of the starch solution was cooked at 95 °C for 25 min. The tert-butanol (95%) for solvent exchange was purchased from Daejung Chemicals and Metals Co., Korea.

Methods

Production and characterization of CNF

Bleached hardwood kraft pulp (HwBKP) was disintegrated with a laboratory disintegrator at 1% consistency for 5 min before fibrillation. A pretreatment of the pulp (beating treatment) was not applied because it was found that the mechanical pretreatment by a beater was not necessary for the production of CNF, if a grinder is used to fibrillate the pulp fibers (Yong *et al.* 2015). A wet disk mill (Supermasscolloider MKCA6-2, Masuko Sangyo, Japan) was used for the fibrillation. The rotational speed was set to 1800 rpm, and the gap clearance between the two disks was reduced to -150 μm from the zero position where the disks began to rub. The pulp consistency was adjusted to 1% (w/w), and the fibrillated materials were collected after 15 passes, 25 passes, and 35 passes, which were named as CNF-15p, CNF-25p, and CNF-35p, respectively. The viscosities of the manufactured CNFs were measured at 1% solids with a Brookfield RVDV-II viscometer (Brookfield AMETEK, USA) at 60 rpm by a Vane-spindle (V73) at 25 °C. The charge density of the CNF was determined by means of a particle charge detector (Mütek PCD 03, BTG Instruments, Germany), which was described by Junka *et al.* (2013). The zeta-potential tests of the CNFs were conducted with the Zetasizer NanoZS Instrument

(Malvern, UK) at 25 °C. The degrees of crystallinity of the CNFs were calculated from X-ray diffraction profiles (Iwamoto *et al.* 2007). These CNFs were then diluted to 0.1% with distilled water and dispersed by an ultrasonic treatment for 30 s with an output frequency of 20 kHz, in preparation for the flocculation experiments.

Particle size analysis

A Malvern Mastersizer 2000 (Malvern Instruments Ltd., UK) instrument equipped with a Hydro 2000S wet dispersion accessory was used to measure the particle size as well as the particle-size distribution. This instrument uses the Frauenhofer diffraction and Mie scattering theories to calculate the particle size (Gaudreault *et al*. 2009). The refractive index of the PCC used was 1.572. The average floc size of PCC and PCC/polymer systems was obtained from five measurements, with a stirring rate of 1500 rpm and no ultrasound.

Photometric dispersion analyzer experiments

A photometric dispersion analyzer (PDA 2000, Rank Brothers, Cambridge, UK) monitored the changes in the state of the PCC aggregation. The details of the PDA technique and its setup can be found in previous literature (Gregory 2004). The PCC suspension was pumped from a 1-L beaker through a transparent 3-mm-diameter tube into the measuring cell of the PDA, which monitors the fluctuations in intensity of transmitted light. As the suspension passes through the PDA light detector, the apparatus measures and calculates several values, including the turbidity and the distribution of particles in a 1-mm^2 cross-sectional area. The data was obtained as the ratio of the RMS / DC signal over time (Eq. 1),

$$Ratio = RMS \;/\; DC \tag{1}$$

where RMS refers to the root mean square of the fluctuations in the transmitted light, and DC refers to the average transmittance. The ratio signal is an indirect measure of the level of flocculation, where higher values usually imply that larger flocs are present.

During the flocculation tests, the stirring speed was kept constant at 300 rpm, and the suspension was circulated at the flow rate of 100 mL/min. In the one-component systems, one type of the CNFs or polyelectrolytes was added to the slurry at 50 s and then mixed for additional 300 s. In the two-component systems, CNF-35p was used as a representative example in the experiment. The C-starch was added at 500 s after the CNF addition and mixed for an additional 1000 s.

The deflocculation and reflocculation experiments for the one-component systems were conducted by altering the stirring speed repeatedly between 300 rpm and 900 rpm every 100 s, for a total of 750 s (Yoon and Deng 2004). The deflocculation and reflocculation experiments for the two-component systems were performed by altering the stirring speed repeatedly between 900 rpm and 300 rpm. The first deflocculation experiment was carried out after 300 s from the addition of C-starch, then deflocculation was carried out for 100 s repeatedly, and the reflocculation was conducted repeatedly for 300 s, for a total of 1300 s. The concentration of the slurry was 0.1% (w/w) and the pH in all of the systems was 8. No salt was added.

Field-emission SEM analysis

Conventional PCC and PCC that had been flocculated by polymers or CNF were dried in a conventional laboratory oven at 105 °C. With respect to the PCC-CNF aggregates, the water in the PCC-CNF aggregates was replaced by tert-butanol; then, the aggregates were freeze-dried by a freeze-dryer (FDB-5505, Operon Co., Korea) at -50 °C. The dried samples of PCC and PCC-CNF aggregates were observed by a field emission scanning electron microscope (S-4300/Hitachi Ltd., Japan).

RESULTS AND DISCUSSION

Flocculation of PCC with CNFs

It is well known that numerous chemicals trigger PCC aggregation. Figures 1a and 1b present the flocculation kinetics of PCC with various polyelectrolytes and CNF-35p, the dosages of which were controlled to 1% on the PCC weight. The ratio signal is an indirect measure of the level of flocculation, and higher values usually imply larger flocs. This is because the flocculation of PCC particles forms larger aggregates, which allow more light to pass intermittently through the suspension to the detector. The PAMs and C-starch were used as references.

Figure 1a shows that the CPAM with the high molecular weight (CPAM-H) produced a greater degree of flocculation than the CPAM of lower molecular weight (CPAM-L). The PCC flocculation with CPAM-H showed the fastest growth before reaching a flocculation plateau at approximately 200 s. The aggregation that was induced by CPAM-H had the largest average particle size, as shown in Fig. 1b. The CPAM with a high molecular weight and high-charge density possibly flocculated the PCC through the bridging mechanism, which was the one of common retention systems used in papermaking.

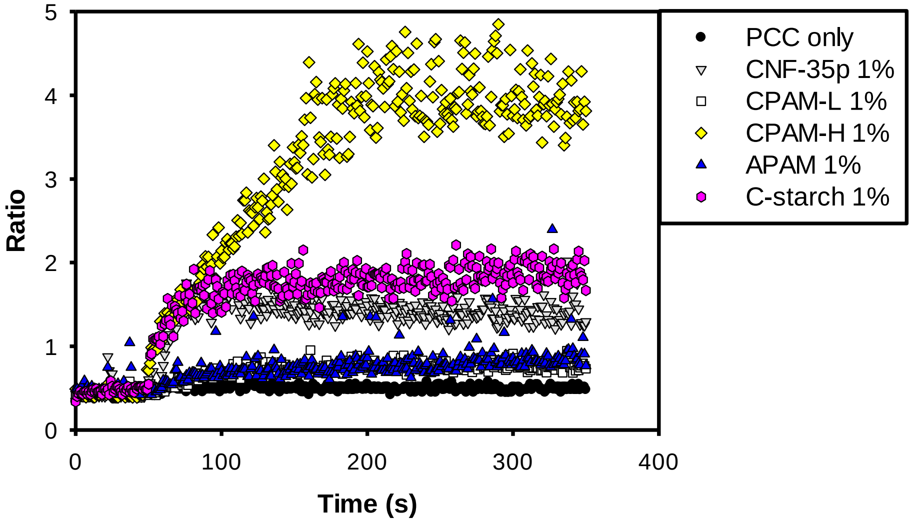
It should be noted that although the average zeta potential of the PCC particle is positive, the PCC surface is actually amphoteric because of the presence of CO_3^{2-} and Ca^{2+} ions (Ono and Deng 1997). Therefore, the CPAM could adsorb onto the PCC surface from water even though both of them were positively charged.

Nevertheless, the CPAM with lower molecular weight caused less flocculation, as shown in Fig. 1b. This result might occur because the length of the polymer chain of the CPAM-L was shorter than the CPAM-H and thus the extension of polymer tails was shorter when adsorbed on the filler surface. As a result, the flocculation ability of CPAM-L was lower than that of CPAM-H.

In the case of APAM, although the flocculation rate was slow and the arrival time of maximum flocculation was over 350 s (Table 2), the APAM flocculated the PCC effectively and created very large aggregates (Fig. 1b). The aggregation induced by the APAM with a dosage of 0.1% was the second largest, followed by the C-starch. The C-starch, which are known to cluster (Gaudreault *et al.* 2009), gave faster flocculation rates than the PAMs (Table 2) and larger flocs than the CPAM-L and CNF-35p (Fig. 1b) because the polymer clusters enlarged the effective size of polymer, leading to larger flocs.

The CNF-35p had a similar trend with C-starch in the initial stage of flocculation, and the maximum flocculation was achieved at about 85 s after the CNF addition (Table 2). Since the flocculation was fast, it was probable that the flocculation occurred mainly through electrostatic interaction (Mahlambi *et al.* 2012). However, the aggregation size induced by the CNF was very small, which was similar to CPAM-L (Fig. 1b). This could be explained by the PCC flocs formed by the CNF that broke under high shear (1500 rpm) during the particle size measurement, due to the weak interactions between PCC particles and CNFs.

(a)



(b)
Particle size distribution

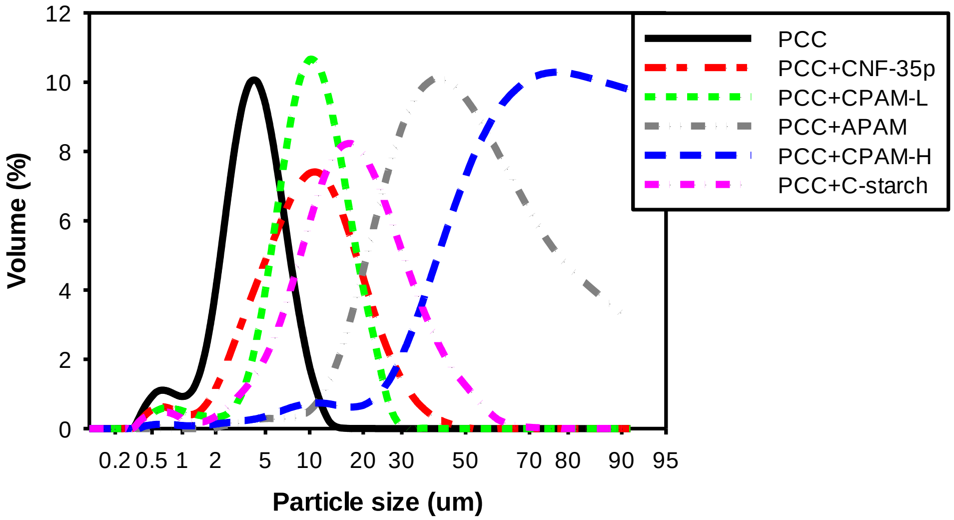


Fig. 1. (a) Flocculation level (ratio) of PCC with various polyelectrolytes and CNF-35p with the dosage of 1% as a function of time; (b) particle size distribution of PCC and PCC flocculated by polyelectrolytes or CNF-35p with a dosage of 0.1%

More detailed analyses of the PCC flocculation with CNFs are given in Figs. 2 and 3. Figure 2 presents the effects of the various degrees of fibrillation of CNFs on PCC flocculation as a function of time. The experiment was carried out at both low (1%) and high (5%) dosages of CNFs.

The flocculation induced by all types of CNFs started almost instantly after the CNF addition, and the maximum flocculation was achieved between 80 and 103 s (Table 2). There was no noticeable difference in the ratio signals for the maximum flocculation among the three types of CNFs (CNF-15p, CNF-25p, and CNF-35p) in both low and high dosages.

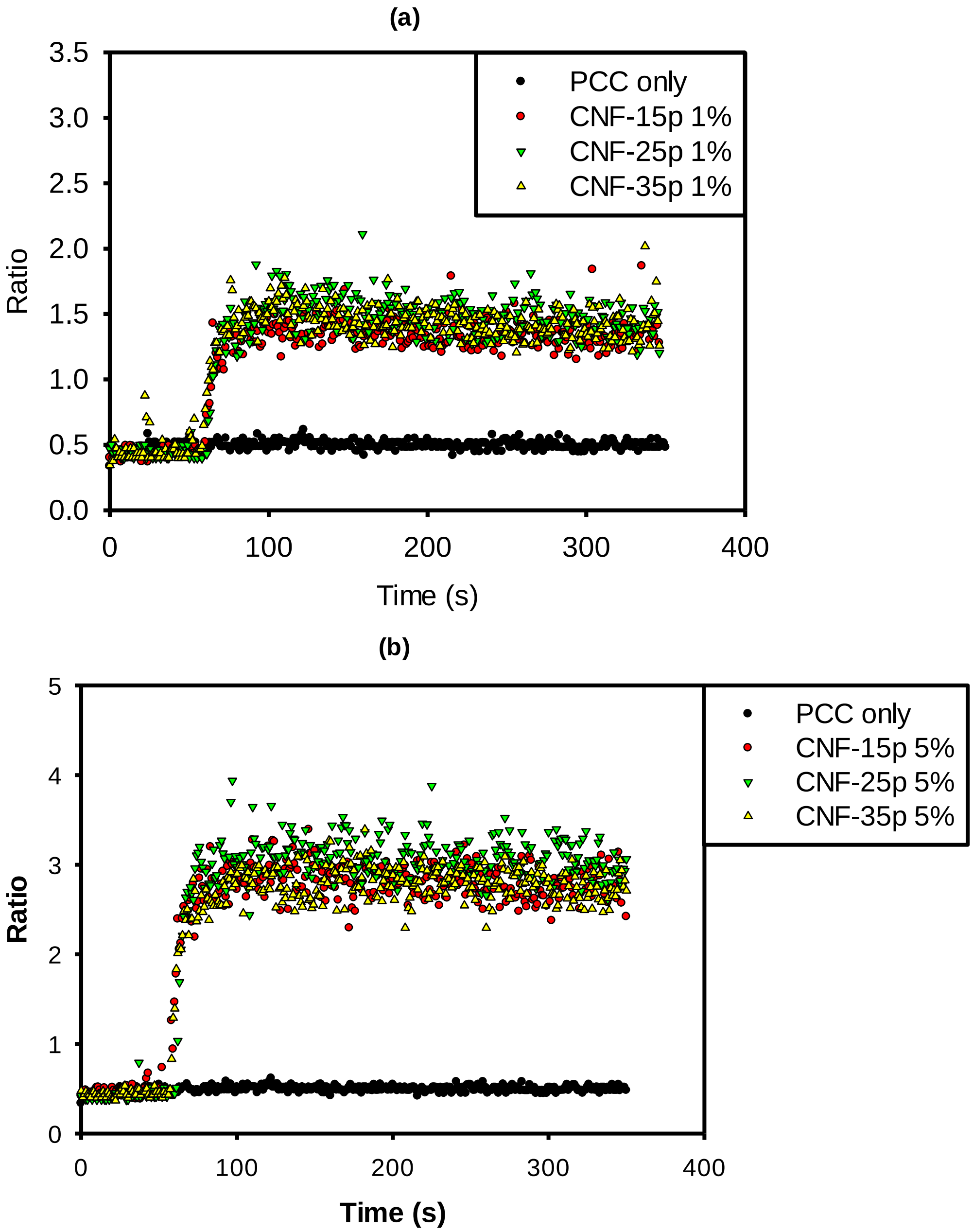


Fig. 2. Flocculation level (ratio) of PCC with CNFs of various degrees of fibrillation as a function of time: (a) with a low dosage of 1%; (b) with a high dosage of 5%

Table 1 presents the characterization of the three types of CNFs produced in this study. An increase in the viscosity and a slight decrease in the zeta potential, charge density, and degree of crystallinity of CNF were found from 15 passes to 35 passes through the grinder. It is well known that during the grinding process, the shearing force generated by the grinding stones degrades the fibers simultaneously with fibrillation. Thus the dimension, the degree of crystallinity, and the degree of polymerization of cellulose fibrils decrease as the number of passes through the grinder increases (Iwamoto *et al.* 2007). Because CNFs with higher aspect ratios have a higher viscosity value (Iwamoto *et al.* 2013), the increase in the viscosity of CNFs from 15 passes to 35 passes indicates that the CNFs used in this experiment had an increased degree of fibrillation.

Table 1. Characterization of CNFs

Sample	Viscosity (mPa·s) at 1% conc.	Zeta Potential (mV)	Charge Density (μeq/g)	Degree of Crystallinity (%)
CNF-15p	293	-33.6 ± 0.6	-94.2	62.3
CNF-25p	610	-34.8 ± 0.3	-101.3	60.3
CNF-35p	795	-36.1 ± 0.6	-126.9	59.5

Table 2. Arrival Times and Average Ratios of Maximum Flocculation from Various CNFS and Polymers

Sample	Arrival Time of Maximum Flocculation (s)	Average Ratio of Maximum Flocculation
1% CPAM-HMW	213 ± 5	4.0 ± 0.33
1% CPAM-LMW	162 ± 5	0.76 ± 0.05
1% APAM	> 350	- -
1% C-starch	93 ± 5	1.80 ± 0.15
1% CNF-15p	90 ± 5	1.39 ± 0.19
1% CNF-25p	88 ± 5	1.47 ± 0.20
1% CNF-35p	85 ± 5	1.44 ± 0.12
5% CNF-15p	92 ± 5	2.82 ± 0.18
5% CNF-25p	98 ± 5	2.97 ± 0.21
5% CNF-35p	95 ± 5	2.8 ± 0.17

Initially, it was hypothesized that the flocculation efficiency of PCC by CNF would increase with the degree of fibrillation, accompanied with the increased aspect ratio and charge properties. However, no noticeable difference in the ratio values was observed in both low and high dosages of CNFs. This result might be due to the imperceptible change of CNFs (Table 1) during the fibrillation process from 15 passes to 35 passes, and also because of the relatively weak interaction between the PCC particles and CNFs. Considering the energy cost in the production of CNFs and the dewatering difficulties caused by CNFs in papermaking applications, these results indicated that it was important to fibrillate fibers at an optimum degree for a given application rather than the maximum degree.

Figure 3a shows the effect of the CNF dosage (based on a PCC solid weight) on the PCC flocculation kinetics. The ratio values increased with an increase in the dosage of CNF. Relatively lower standard deviations of ratio values were observed at lower dosages of CNF (below 1%), as shown in Fig. 3b, which implied that the flocculations of the PCC were stable and the flocs sizes formed were uniform. Under this circumstance, the breakage and reflocculation of the PCC flocs eventually balanced out and the aggregates reached a stable size and structure. In contrast, higher standard deviations of the ratio values were observed at higher dosages of CNF (above 1%), which implied that the flocculations were unstable and the floc formed were irregular. As mentioned, CNF is known to have a high aspect ratio and a high surface area, and they already form a network at heavily diluted aqueous suspensions (Salmi *et al.* 2009). The CNF, which shows a negative charge, possesses carboxyl groups originating mainly from the residual hemicelluloses in pulp, with a small amount attributable to cellulose oxidation during the pulping operation (Olszewska *et al.* 2011). The quite broad effective dosing range might be due to the low charge density of CNF, as shown in Table 1. Also, as shown in Fig. 3b, the slope of the curve was relatively steeper under the CNF dosage of 2%, meaning that the flocculation rate was relatively high. Then, the flocculation rate slowed down beyond the 2% CNF dosage. This might occur because more CNF adsorption led to a reduction in the electrostatic repulsion between the positive PCC particles, allowing the attractive van der Waals forces to become dominant. It can be predicted that the flocculation might reach a maximum at a higher dosage than 10%, even though it was not shown in this work. These results were similar to the findings by Chen and Van de Ven 2016. This flocculation behavior was similar to the polymer bridging theory.

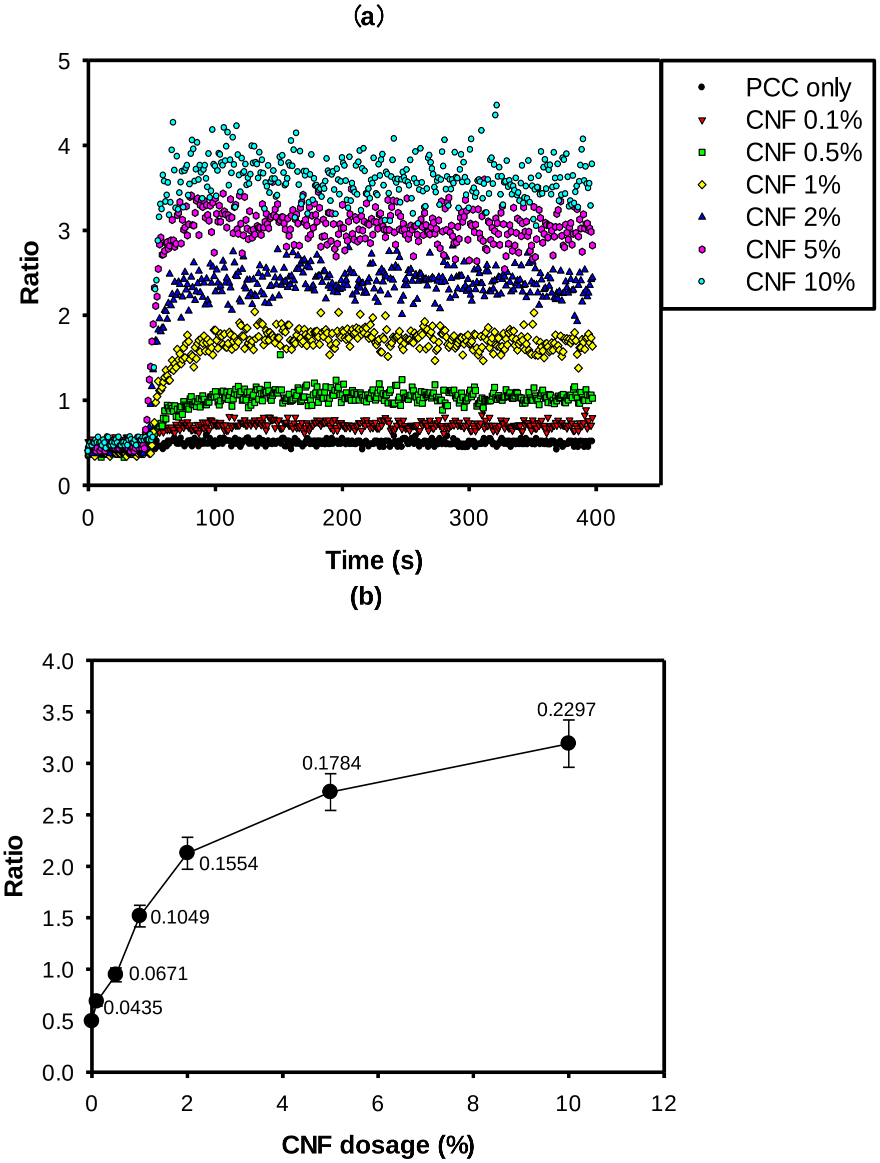


Fig. 3. Effect of the dosage of CNF-35p (based on a PCC solid weight) on the PCC flocculation level: (a) ratio as a function of time; (b) ratio as a function of CNF-35p dosages (standard deviations were quantified)

The reversibility of the PCC flocculation with CNF as a flocculant was studied. As shown in Fig. 4, the CNF showed a noticeable reflocculation capability. The shear conditions were altered between 300 and 900 rpm every 100 s. When the PCC aggregates caused by the CNF were exposed to a high shear level (900 rpm), the ratio signal of the PCC suspension decreased suddenly, indicating the breakage of flocs. When the shear condition was lowered back to 300 rpm, the ratio signal increased immediately, indicating that the broken flocs were reflocculated intensely. After several high shear stages, the reflocculation of PCC still stayed relatively noticeable, at over 80% reversibility, meaning that the dispersed flocs formed again and the floc size was over 80% of the initial floc size. As previously mentioned, reflocculation can rapidly take place only in the case of patch flocculation. In contrast, very weak reversibility can usually be seen in the flocculants that function using the bridging theory (Norell *et al.* 1999). In fact, the CNFs appeared like aggregated bundles that consisted of thin wire-like microfibrils with diameters of a few nanometers, which was different from the common bridging flocculants such as synesthetic polyelectrolytes. When common synthetic polymer bridging flocculants are exposed to a high shear, the polymer chains break or transfer from one particle surface to the other particle surface and the PCC flocs become smaller with repeating flocculation and deflocculation, resulting in a lower flocculation reversibility. Cellulose nanofibrils, which have a large specific surface area and a high aspect ratio, can flocculate PCC particles primarily through bridging. However, the CNF seems to be insensitive to the increase of the shearing force, meaning that few conformations or few cleavage events of CNF occurred under a high shear, which might be due to its excellent mechanical properties. Therefore, the reflocculation could rapidly take place when the shearing action stopped.

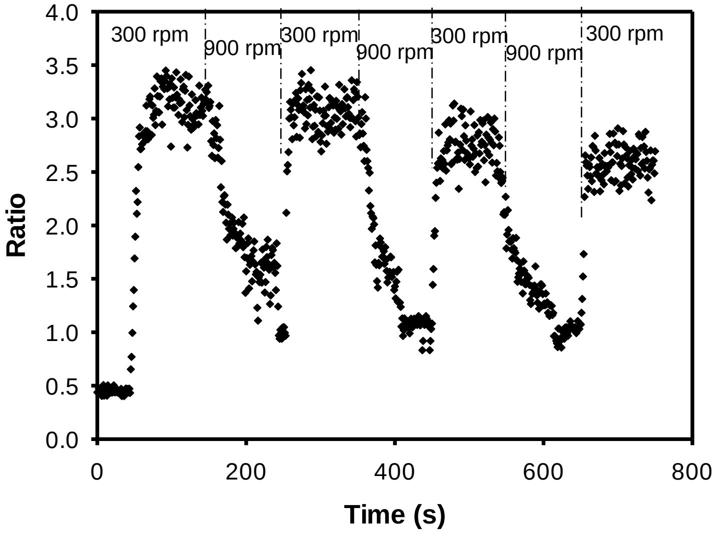
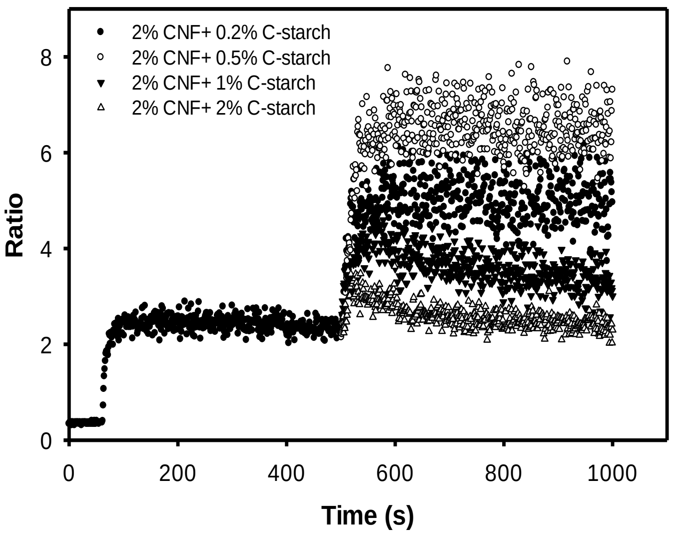


Fig. 4. Flocculation level (ratio) and re-flocculation level of PCC with CNF (5%) as a function of time

Flocculation of PCC with Two-Component Systems

In general, single component systems are not the most efficient way to flocculate particles. Therefore, several different multicomponent systems have been studied in the past (Shen *et al.* 2010; Cho *et al.* 2011). Starch is a kind of polymer of D-glucose with α-linkages that has been commonly used in papermaking. C-starch has been found highly effective in the filler flocculation, and it can be anchored on the filler surfaces or used to encapsulate the filler particles to enhance fiber-filler bonding, and to improve the strength properties of filled papers (Chauhan and Bhardwaj 2014). Therefore, the flocculation of PCC by two kinds of carbohydrate-based polymers (CNF and C-starch) was also studied.

(a)



(b)

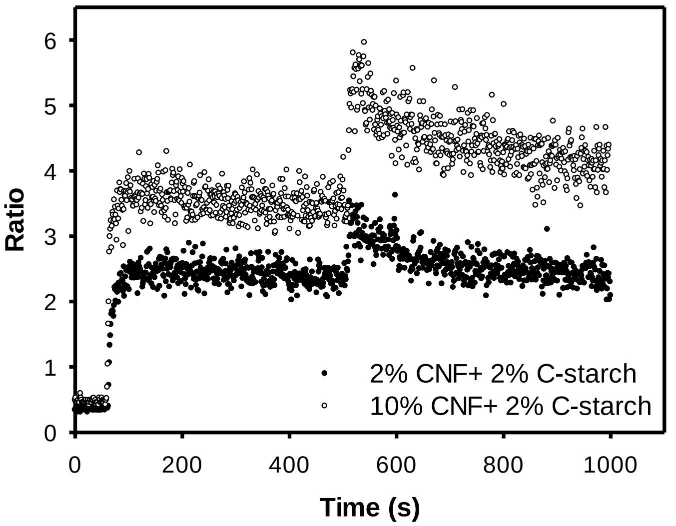


Fig. 5. Flocculation level (ratio) of PCC with (a) CNF (2% addition on PCC) and C-starch (four addition levels: 0.2%, 0.5%, 1%, and 2%); (b) CNF (two addition levels: 2% and 10%) and C-starch (2% addition on PCC) CNF-35p was used and the stirring speed was controlled to 300 rpm

In this study, the CNF was added first at 50 s and then the C-starch was added after mixing for 450 s. Figures 5a and 5b present the PCC flocculation kinetics with two-component systems, where the CNF and C-starch were sequentially added to the PCC suspension (additions at 50 s and 500 s). In Fig. 5a, the added amount of CNF was 2%, while the dosage of the C-starch varied from 0.2% to 2%. After the addition of 2% CNF, a relatively equable maximum flocculation was obtained, but the ratio value was low. Higher ratios of the PCC flocculation arose after the C-starch addition. This might be explained by the fact that the C-starch could efficiently adhere on the PCC aggregates that were bridged with the anionic charged CNF and form larger aggregates. Another possible reason might be that the free CNFs in the suspension could form complexes with the C-starch and the complex could work as a flocculant, increasing the flocculation efficiency. Eronen *et al.* (2012) found that the C-starch had high-adsorbed mass and energy dissipation with the anionic CNFs, indicating the formation of a coiled, loose, gel-like multilayer structure. Because of this, the CNFs may form long networks with the C-starch and cause more efficient flocculation. The largest efficient flocculation was achieved at a 0.5% C-starch addition. Only a slight increase in the ratio signal was observed when the C-starch dosage was increased to 2% on the PCC weight, indicating a weak flocculation of the PCC particles. From these results, it seemed that the net charges of the added polymers also played a role in the PCC flocculation tendency in two-component systems. According to the given charge densities of CNF and C-starch, the net charge was clearly cationic when the C-starch dosage was 2%, and it was about neutral with 1% dosage of C-starch while it was clearly anionic with 0.2% and 0.5% dosages of C-starch. Moreover, a relatively intensive increase in the ratio signal was observed when the initial CNF dosage increased from 2% to 10% (Fig. 5b), indicating a strong flocculation of the PCC particles. These results imply that sufficient dosages of anionic CNFs, which adsorbed on the PCC surface or remained free to obtain an anionic charge in suspension, are needed to achieve an efficient flocculation in a two-component system.

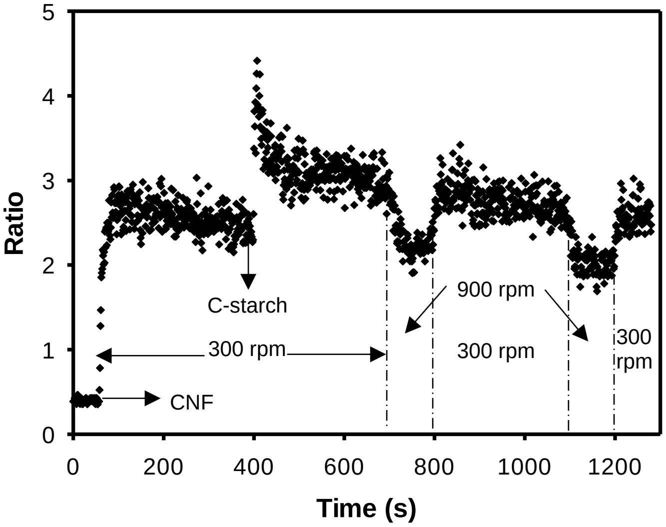


Fig. 6. Flocculation level (ratio) and re-flocculation level of PCC with 2% CNF and 1% C-starch as a function of time

As shown in Fig. 6, the re-flocculation of PCC with a two-component system was also studied. A noticeable re-flocculation capability was observed with the two-component system. Compared with the case that the PCC flocculated by CNF (Fig. 4), when the PCC flocs were exposed to the high shear level (900 rpm), the PCC flocs with two components were broken and the ratio value remained at approximately 2 (Fig. 6). In contrast, the ratio value of broken PCC flocs with the single CNF system was decreased to approximately 1. These results imply that the two-component system using CNF and C-starch provided stronger interactions between the PCC particles than the CNF single system, maintaining the bonds between the PCC particles under a high shear level. The two-component system also showed high flocculation reversibility. In fact, initial floc properties, mainly size and structure, which are conditioned by the course of flocculation, play a crucial role in the reflocculation stage, the larger aggregates formed by a two-component system consisted of CNFs and C-starch would result in a better filler retention. It seems to be more appropriate to use the two-component system in the paper manufacturing process.

Morphology of PCC Flocculated by Polymers and CNF

The morphological characteristics of PCC particles and PCC particles flocculated by polymers/CNF were compared using SEM images (Fig. 7).

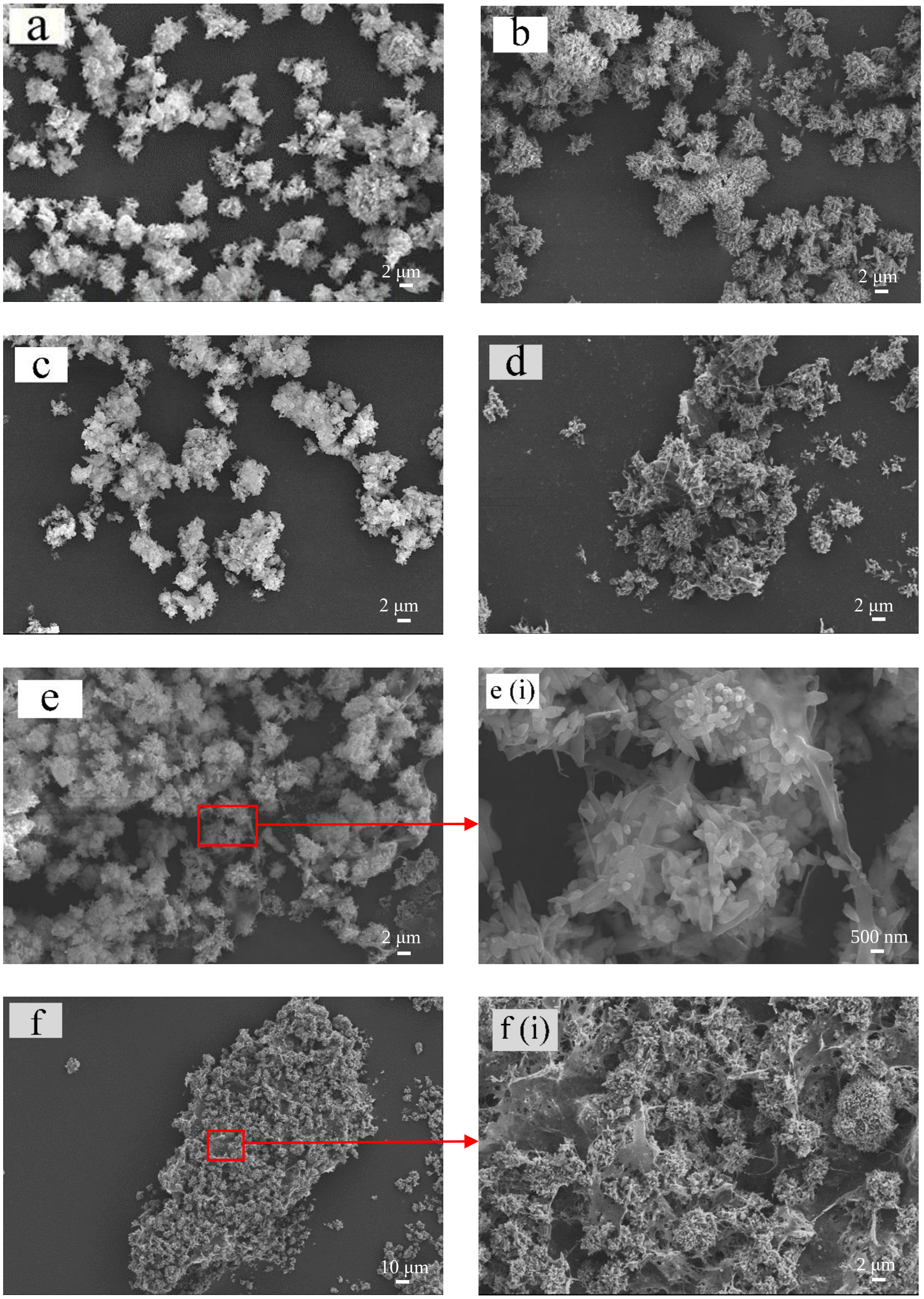


Fig. 7. SEM images: (a) conventional PCC, (b) PCC flocculated by CPAM-H (0.1%), (c) PCC flocculated by C-starch (0.1%), (d) PCC flocculated by CNF-35p (5%) with oven drying, (e) PCC flocculated by CNF-35p (5%) with freeze-dried drying, (f) PCC flocculated by two-component systems: CNF-35p (10%) and C-starch (2%)

The conventional PCC particles, which had the scalenohedral structure, were comparatively regular in shape with little aggregates within the narrow size range. In contrast, the PCC flocculated by the CPAM-H or C-starch had more and larger aggregates than the conventional PCC particles (Figs. 7a, b, and c).

Figures 7d and e show the morphology of PCC particles that were flocculated by CNF-35p, which was dried by oven-drying and freeze-drying, respectively. Because of the strong intermolecular hydrogen bonds developed during a drying stage, a continuous CNF-PCC network and a relatively bulky structure were formed. A more distinct morphology of PCC flocculated by CNF can be seen in Fig. 7e. Under the high magnification of 10000× in Fig. 7e(i), it is apparent that the CNF fibril loops were adsorbed onto the PCC particle surface in a conformation where the loops and tails of the fibrils extend away from the PCC particle surface. These loops or tails attached themselves to another particle surface when an inter-particle collision occurred to form a bridge between the two PCC particles. These results support the hypothesis that the flocculation mechanism between the PCC and CNF is bridging/networking. Figure 7f showed the morphology of the PCC particles that were flocculated by a two-component system (10% CNF addition and 2% C-starch addition). The larger aggregates formed and under a high magnification of 2000×, the CNFs were firmly embedded into the PCC matrix, as shown in Fig. 7f (i).

CONCLUSIONS

1. Cellulose nanofibrils are nano-sized cellulosic materials with unique properties, and the PDA results showed that CNFs can be used to flocculate particles such as calcium carbonate fillers. The SEM images showed that the CNFs functioned as bridges between the two PCC particles. However, the PCC floc is easily broken under a high shear level due to the weak interaction between the PCC particles and CNFs.
2. The degree of fibrillation did not noticeably influence the PCC flocculation in this experiment. This indicated that it was important to fibrillate fibers at an optimum degree rather than the maximum degree in papermaking applications when considering the energy cost in the production of CNFs and the dewatering difficulties caused by CNFs.
3. Although the synthetic polymers are much more effective than the CNFs because of their versatile tailorability, a noticeable reflocculation capability was observed in one- and two-component systems that consisted of CNFs. This indicates that few conformations or few cleavages of CNFs occurred under a high shear level because of their excellent mechanical properties. This is different from common bridging flocculants, such as synthetic polyelectrolytes, which have poor shear stability and little biodegradability.
4. The flocculation efficiency was improved when the CNFs were combined with C-starch in a two-component system. C-starch in a two-component system with CNFs can efficiently consolidate the formation of CNF bridges between PCC particles and form larger aggregates. For a better filler retention, it seems to be more appropriate to use a two-component system consisted of CNFs and C-starch in the paper manufacturing process.

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REFERENCES CITED

Biswal, D. R., and Singh, R. P. (2006). "Flocculation studies based on water-soluble polymers of grafted carboxymethyl cellulose and polyacrylamide," *Journal of Applied Polymer Science* 102(2), 1000-1007. DOI 10.1002/app.24016

Cai, H., Sharma, S., Liu, W., Mu, W., Zhang, X., and Deng, Y. (2014). "Aerogel microspheres from natural cellulose nanofibrils and their application as cell culture scaffold," *Biomacromolecules* 15(7), 2540-2547. DOI: 10.1021/bm5003976

Chakraborty, A., Sain, M., and Kortschot, M. (2005). "Cellulose microfibrils: A novel method of preparation using high shear refining and cryocrushing," *Holzforschung* 59(1), 102-107. DOI: 10.1515/HF.2005.016

Chauhan, V. S., and Bhardwaj, N. K. (2014). "Cationic starch preflocculated filler for improvement in filler bondability and composite tensile index of paper," *Industrial and Engineering Chemistry Research* 53(29), 11622-11628. DOI: 10.1021/ie502008d

Chen, D. Z, and Van de Ven, T. G. M. (2016). "Flocculation kinetics of precipitated calcium carbonate induced byelectrosterically stabilized nanocrystalline cellulose," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 504, 11-17. DOI: 10.1016/j.jcis.2007.01.031

Cho, B. -U, Kim, H. J., and Won, J. M. (2011). "Production of high loaded paper by dual flow additions of fillers: (I) Effects of filler addition at thick stock on paper properties and papermaking process," *Journal of Korea TAPPI* 43(4), 23-30.

Dimic-Misic, K., Gane, P. A. C., and Paltakari, J. (2013). "Micro- and cellulose nanofibrils as a rheology modifier additive in CMC-containing pigment-coating formulations," *Industrial and Engineering Chemistry Research* 52(45), 16066-16083. DOI: 10.1021/ie4028878

Eichhorn, S., Dufresne, A., Aranguren, M., Marcovich, N., Capadona, J., Rowan, S., Weder, C., Thielemans, W., Roman, M., Renneckar, S., *et al.* (2010). "Review: Current international research into cellulose nanofibres and nanocomposites," *Journal of Materials Science* 45(1), 1-33. DOI: 10.1007/s10853-009-3874-0

Eronen, P., Laine, J., Ruokolainen, J., and Österberg, M. (2012). "Comparison of multilayer formation of different cellulose nanofibrils and cationic polymers," *Journal of Colloid and Interfacial Science* 373(1), 84-93. DOI: 10.1016/j.jcis.2011.09.028

Gaudreault, R. N., Cesare, N. D., Weitz, D., and Van de Ven, T. G. M. (2009). "Flocculation kinetics of precipitated calcium carbonate," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 340, 56-65. DOI:10.1016/j.colsurfa.2009.03.008

Gregory, J. (2004). "Monitoring floc formation and breakage," *Water Science and Technology* 50(12), 163-170.

He, M., Lee, Y. K., and Won, J. M. (2015). "Effect of the modification of PCC with NCC on the paper properties," *Journal of Korea TAPPI* 47, 136-143. DOI: 10.7584/ktappi.2015.47.4.136

He, M., Cho, B. U., and Won, J. M. (2016). "Effect of precipitated calcium carbonate-cellulose nanofibrils composite filler on paper properties," *Carbohydrate Polymers* 136, 820-825. DOI: 10.1016/j.carbpol.2015.09.069

Henriksson, M., Henriksson, G., Berglund, L., and Lindstrom, T. (2007). "An environmentally friendly method for enzyme-assisted preparation of microfibrillated cellulose (MFC) nanofibers," *European Polymer Journal* 43(8), 3434-3441. DOI:10.1016/j.eurpolymj.2007.05.038

Henriksson, M., Berglund, L., Isaksson, P., Lindström, T., and Nishino, T. (2008). "Cellulose nanopaper structures of high toughness," *Biomacromolecules* 9(6), 1579-1585. DOI: 10.1021/bm800038n

Hubbe, M., Rojas, O. J., Lucia, L. A., and Sain, M. (2008). "Cellulosic nanocomposites: A review," *BioResources* 3(3), 929-980. DOI: 10.15376/biores.3.3.929-980

Iwamoto, S., Nakagaito, A., N., and Yano, H. (2007). "Nano-fibrillation of pulp fibers for the processing of transparent nanocomposites," *Applied Physics A-Materials Science and Processing* 89(2), 461-466. DOI: 10.1007/s00339-007-4175-6

Iwamoto, S., Abe, K., and Yano, H. (2008). "The effect of hemicelluloses on wood pulp nanofibrillation and nanofiber network characteristics," *Biomacromolecules* 9(3), 1022-1026. DOI: 10.1021/bm701157n

Iwamoto, S., Lee, S., and Endo, T. (2013). "Relationship between aspect ratio and suspension viscosity of wood cellulose nanofibers," *Polymer Journal* 46(1), 73-76. DOI:10.1038/pj.2013.64

Jin, L. Q., Wei, Y. W., Xu, Q. H., Yao, W. R., and Cheng, Z. L. (2014). "Cellulose nanofibers prepared from TEMPO-oxidation of kraft pulp and its flocculation effect on kaolin clay," *Journal of Applied Polymer Science* 131(12), 1-8. DOI: 10.1002/app.40450

Junka, K., Filpponen, I., Lindström, T., and Laine, J. (2013). "Titrimetric methods for the determination of surface and total charge of functionalized nanofibrillated/ microfibrillated cellulose (NFC/MFC)," *Cellulose* 20(6), 2887-2895. DOI: 10.1007/s10570-013-0043-z

Kajanto, I., and Kosonen, M. (2012). "The potential use of micro- and nanofibrillated cellulose as a reinforcing element in paper," *Journal of Science and Technology for Forest Products and Processes* 6(2), 42-48.

Kwon, O. K., and Shin, S. J. (2016). "Electron microscopy for the morphological characterization of nanocellulose materials," *Journal of Korea TAPPI* 48(1), 5-18. DOI: 10.7584/ktappi.2016.48.1.005

Liimatainen, H., Sirviö, J., Sundman, O., Visanko, M., Hormi, O., and Niinimäkia, J. (2011). "Flocculation performance of a cationic biopolymer derived from a cellulosic source in mild aqueous solution," *Bioresource Technology* 102(20), 9626-9632. DOI:10.1016/j.biortech.2011.07.099

Mahlambi, M., Mishra, A., Mishra, S., Krause, R., Mamba, B., and Raichur, A. (2012). "Synthesis and characterization of carbon-covered alumina (CCA) supported TiO_2 nanocatalysts with enhanced visible light photodegradation of Rhodamine B," *Journal of Nanoparticle Research* 14(4), 790-801. DOI: 10.1007/s11051-012-0790-z

Norell, M., Johansson, K., and Persson, M. (1999). "Retention and drainage," in: *Papermaking Chemistry*, L. Neimo (ed.), Fapet Oy, Helsinki, pp. 42-81.

Olszewska, A., Eronen, P., Johansson, L. S., Malho, J. M., Ankerfors, M., Lindström, T., Ruokolainen, J., Laine, J., and Österberg, M. (2011). "The behaviour of cationic nanofibrillar cellulose in aqueous media," *Cellulose* 18(5), 1213-1226. DOI: 10.1007/s10570-011-9577-0

Ono, H., and Deng, Y. (1997). "Flocculation and retention of precipitated calcium carbonate by cationic polymeric microparticle flocculants," *Journal of Colloid and Interface Science* 188(1), 183-192. DOI:10.1006/jcis.1997.4766

Pääkko, M., Ankerfors, M., Kosonen, H., Nykänen, A., Ahola, S., Österberg, M., Ruokolainen, J., Laine, J., Larsson, T., Ikkala, O., *et al*. (2007). "Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels," *Biomacromolecules* 8(6), 1934-1941. DOI: 10.1021/bm061215p

Petersson, L., and Oksman, K. (2006). "Comparing layered silicates and microcrystalline cellulose as nano-reinforcement," *Composites Science and Technology* 66(13), 2187-2196. DOI:10.1016/j.compscitech.2005.12.010

Roy, D., Semsarilar, M., Guthrie, J. T., and Perrier, S. (2009). "Cellulose modification bypolymer grafting: A review," *Chemical Society Review* 38(7), 2046-2064. DOI: 10.1039/B808639G

Saito, T., Nishiyama, Y., Putaux, J., Vignon, M., and Isogai, A. (2006). "Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose," *Biomacromolecules* 7(6), 1687-1691. DOI: 10.1021/bm060154s

Salmi, J., Nypelö, T., Österberg, M., and Laine, J. (2009). "Layer structures formed by silica nanoparticles and cellulose nanofibrils with cationic polyacrylamide (C-PAM) on cellulose surface and their influence on interactions," *BioResources* 4(2), 602-625. DOI: 10.15376/biores.4.2.602-625

Shen, J., Song, Z., Qian, X., and Song, C. (2008). "Chitosan-coated papermaking grade PCC filler prepared by alkali precipitation: Properties and application," in: *Proceedings from the 2nd International Papermaking and Environment Conference,* Tianjin, China, pp. 645-650.

Shen, J., Song, Z., Qian, X., and Yang, F. (2010). "Carboxymethyl cellulose/alum modified precipitated calcium carbonate fillers: Preparation and their use in papermaking," *Carbohydrate Polymers* 81(3), 545-553. DOI:10.1016/j.carbpol.2010.03.012

Shogren, R. L. (2009). "Flocculation of kaolin by waxy maize starch phosphates," *Carbohydrate Polymers* 76(4), 639-644. DOI:10.1016/j.carbpol.2008.11.027

Suopajärvi, T., Liimatainen, H., Hormi, O., and Niinimäki, J. (2013). "Coagulation-flocculation treatment of municipal wastewater based anionized nanocelluloses," *Chemical Engineering Journal* 231(12), 59-67. DOI: 10.1016/j.cej.2013.07.010

Wågberg, L., Decher, G., Norgren, M., Lindström, T., Ankerfors, M., and Axnäs, K. (2008). "The build-up of polyelectrolyte multilayers of microfibrillated cellulose and cationic polyelectrolytes," *Langmuir* 24(3), 784-795. DOI: 10.1021/la702481v

Wang, B., and Sain, M. (2007). "Isolation of nanofibers from soybean source and their reinforcing capability on synthetic polymers," *Composites Science and Technology* 67(11), 2521-2527. DOI:10.1016/j.compscitech.2006.12.015

Yong, S. M., Kwak, G. H., Cho, B. U., Lee, Y. K., and Won, J. M. (2015). "Effects of pulp pre-treatment and grinder clearance on the manufacturing characteristics of microfibrillated cellulose," *Journal of Korea TAPPI* 47(2), 61-69. DOI : 10.7584/ktappi.2015.47.2.061

Yoon, S., and Deng, Y. (2004). "Flocculation and reflocculation of clay suspension by different polymer systems under turbulent conditions," *Journal of Colloid and Interface Science* 278(1), 139-145. DOI:10.1016/j.jcis.2004.05.011

Yoon, S., and Deng, Y. (2006). "Clay-starch composites and their application in papermaking," *Journal of Applied Polymer Science* 100(2), 1032-1038. DOI: 10.1002/app.23007

Zimmermann, T., Bordeanu, N., and Strub, E. (2010). "Properties of cellulose nanofibrils from different raw materials and its reinforcement potential," *Carbohydrate Polymers* 79(4), 1086-1093. DOI: 10.1016/j.carbpol.2009.10.045

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