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# Effect of precipitated calcium carbonate—Cellulose nanofibrils composite filler on paper properties

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ABSTRACT

A new concept of composite filler was developed by using cellulose nanofibrils (CNF), precipitated calcium carbonate (PCC) and cationic starch (C-starch). In this study, cellulose nanofibrils were utilized in two different ways: a PCC–CNF composite filler and a papermaking additive in sheet forming. The aim was to elucidate their effects on flocculation, filler retention and the strength and optical properties of handsheets. The highest filler retention was obtained by using the PCC–CNF composite filler in paper sheets. The paper filled with the composite fillers had much higher bursting and tensile strengths than conventional PCC loading. It was also found that the paper prepared with PCC–CNF composite fillers became denser with increasing the filler content of paper.



## 1. Introduction

Paper is a sheet composite consisting of cellulose-based fibers and additives such as fillers, pigments, sizing agents, and processing aids. In the paper industry synthetic polyelectrolytes have been used for several purposes such as to increase retention of fines and fillers (kaolin, PCC etc.), to improve paper quality and to reduce material and energy costs. Due to environmental issues renewable natural based materials have gained great interest across the globe. Among the numerous methods available in the literature, the use of biodegradable and renewable carbohydrate polymers (such as starch, cellulose, and chitosan) in filler loading is a very interesting and promising research topic. As the common fillers are not capable of forming bonds with fibers, filler combined with carbohydrate polymers enhances the compatibility between fillers and fibers, and confers certain beneficial attributes of carbohydrate polymers to fillers. The advantages of using carbohydrate polymers in filler loading can at least include such aspects as low cost, easy availability and environmental friendliness of the modifiers, enhanced paper strength and improved filler retention (Shen, Song, Qian, & Yang, 2010). Cellulose is the most abundant natural polymer on the earth. Recently, there has been an intense research activity in the field of cellulose nanofibril (CNF) and cellulose microfibril (CMF). Generally, CNF or CMF can be produced by mechanically disintegration such as refining or high-pressure homogenization (Iwamoto, Abe, & Yano, 2008), cryocrushing (Chakraborty, Sain, & Kortschot, 2005), microfluidisation (Zimmermann, Bordeanu, & Strub, 2010), grinding (Abe, Iwamoto, & Yano, 2007; Sim, Ryu, & Youn, 2013; Yong, Kwak, Cho, Lee, & Won, 2015) and high intensity ultrasonication (Petersson & Oksman, 2006) In order to fibrillate fibers effectively, many researchers have combined the mechanical treatment with chemical or enzymatic treatments (Kim, Jung, Jung, Ahn, & Eom, 2015). By these methods, the properties of the fibrils such as their size and surface charge can be modified. Enzymatic pretreatments enable the manufacture of CNF with significantly reduced energy consumption and reduce the fibrils diameter down to below 20 nm range (Pääkko et al., 2007). Another effective method to chemically modify the pulp to produce high charge fibrils is the TEMPO-mediated oxidation, it is a method for surface modification of native celluloses, by which carboxylate and aldehyde functional groups can be introduced into solid native celluloses via 2,2,6,6-tetramethylpiperidine-1-oxyl radical oxidation

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(TEMPO) under aqueous and mild conditions (Saito, Nishiyama, Putaux, Vignon, & Isogai, 2006). In these cases, the oxidation occurred only at the surface of the microfibrils, which became negatively charged. The charged groups prevent the aggregation of fibrils via electrostatic repulsion, thus easing fibrillation.

CNFs manufactured from renewable raw materials have several advantageous basic properties, i.e. high mechanical strength, large specific surface area and high aspect ratios, barrier properties, dimensional stability, biodegradability and biocompatibility (Eichhorn et al., 2010). Due to these properties, they have already shown promising results in several fields such as flocculation and retention of particles (Korhonen & Laine, 2014; Suopajärvi, Liimatainen, Hormi, & Niinimäki, 2013), rheology modification (Dimic-Misic, Gane, & Paltakari, 2013), composite materials (Hubbe, Rojas, Lucia, & Sain, 2008), high strength films (Henriksson, Berglund, Isaksson, Lindström, & Nishino, 2008) and strength addition of paper. Eriksen, Syverud, and Gregersen (2008) found significant tensile index increase at 4% addition of MFC to thermo mechanical pulp (TMP) handsheets independent of the production method, and addition of MFC also increased the air resistance. Mörseburg and Chinga-Carrasco (2009) added MFC to clay loaded layered TMP sheets and found that the strength properties improved. Hii, Gregersen, Chinga-Carrasco, and Eriksen (2012) found that filler-MFC-fiber interactions simultaneously improve both the light scattering and the strength properties of the sheet.

The filler retention also can be increased by using CNF. Ämmälä, Liimatainen, Burmeister, and Niinimaki (2013) found the ground calcium carbonate (GCC) filler retention remained between 85% and 90% with TEMPO nanofibrils. The role of CNFs is similar to the external fibrillation of fiber, because they are able to bridge the filler-induced void in the fiber-fiber bonding domain, acting as a glue strengthening the fiber-filler and filler-filler contacts (Xu & Pelton, 2005). The flocculation of PCC filler with CNF have previously been reported by Korhonen and Laine (2014), the results clearly showed that various CNFs can be used as effective flocculants, and the flocculation mechanism for CNF was not only bridging but more of a hybrid between bridging/networking and the patch flocculation mechanisms.

The presence of polyelectrolytes can strengthen and induce formation of CNF/polyelectrolyte bridges between filler particles, leading to more efficient flocculation. In this study, efficient flocculation between PCC and CNF was achieved by C-starch and the aggregates were called “PCC–CNF composite filler”.

In this paper, cellulose nanofibrils were used in two different ways: a PCC–CNF composite filler and a papermaking additive in sheet forming. The aim was to elucidate the effects of PCC–CNF composite fillers on PCC retention and properties of paper sheets. Filler retention, strength properties, formation and optical properties of the handsheets were evaluated in the experiments.

## 2. Experimental

### 2.1. Materials

Bleached softwood kraft pulp (Radiata pine, Pacifico Pulp, Chile), Bleached hardwood kraft pulp (Acacia, April, Indonesia) and PCC (Hankuk Paper Ltd., Korea) were used as raw materials for this study. Dried PCC was suspended in tap water to obtain solids content of 15% (w/w) without using any dispersion agents. The mean size of PCC (Scalenohedral type) was 2.2 μm. A microparticle system consisted of poly-aluminum chloride (PAC, concentration 12%, $Al_2O_3$ equivalent 10.5%, percent basicity 44.7%, pH 4.2), anionic polyacrylamide (APAM, charge density (CD) −0.86 meq/g, molecular weight (MW) 1000–1200 × $10^4$ g/mol) and micro-polymer (MP, branched anionic PAM, CD −1.58 meq/g, MW 600–700 × $10^4$ g/mol) were used for filler retention. Cationic starch (C-starch) which had a degree of substitution (DS) of 0.04 was supplied from SamYang Genex Corp, Korea. Before use, 2 g/L of starch solution was cooked at 95 °C for 25 minutes. Tert-Butanol (95%) for solvent exchange was purchased from Daejung Chemicals & Metals Co, Korea.

### 2.2. Methods

#### 2.2.1. CNF production

Bleached hardwood kraft pulp (HwBKP) was beaten to 150 mL CSF (Canadian standard freeness) in a laboratory Valley beater (Toyo selki, JP/123-A, 0.37 kW). A wet disk-milling (Supermasscolloider MKCA6-2, Masuko Sangyo, Japan) was used for fibrillation. The rotational speed was set to 1800 rpm, and the gap clearance between two disks was reduced to −150 μm from the zero position where the disks began to rub. The pulp consistency was adjusted at 1% and the fibrillated materials were collected after 35 passes.

#### 2.2.2. Preparation of PCC–CNF composite filler

CNF gel was diluted with deionized water to 0.1%, mixed with the PCC suspensions with a concentration of 2% and stirred for 5 min at 600 rpm. Then the cooked C-starch solution was added into the mixture and stirred for 5 min at 600 rpm. Large flocs were formed after C-starch addition. CNF dosage of 2% on pulp weight (oven dried, O.D.) was applied, while the dosage of C-starch was 2.5% on PCC weight.

#### 2.2.3. Hand-sheet preparation

Hardwood bleached kraft pulps (HwBKP) and softwood bleached kraft pulps (SwBKP) were beaten to a freeness of 450 mL CSF. The base furnish consisting of HwBKP and SwBKP (80:20) were mixed in a container and then subsequently diluted to 0.5% concentration with tap water. A microparticle system consisting of poly-aluminum chloride (PAC), anionic polyacrylamide (APAM) and micro-polymer (MP) was used for filler retention. The materials were pre-mixed before the sheet-making in the following sequence (Fig. 1): pulps–PAC–filler/composite filler–APAM–M.P. The dosage of PAC, APAM and M.P on pulp weight (oven dry) was 0.6%, 0.015%, and 0.14%, respectively. The dosages of PCC were 20%, 30%, 40% on pulp weight. The time delay between the addition of the retention aids and fillers was 10 s, 10 s, 20 s, and 10 s, respectively. The furnish mixture was stirred rigorously with a stirrer at 1000 rpm during the addition of the retention chemicals. In the experiment for comparison, CNF and C-starch were added into the furnish after the filler addition in following order: pulps–PAC–Filler–CNF–APAM–M.P–C-starch. The dosage of CNF was 2% on pulp weight while the dosage of C-starch was 2.5% on filler weight. 80 g/$m^2$ of hand-sheets were made with a conventional hand-sheet former (DM-830, 250 mm × 250 mm, Daeil Machinery Ltd., Korea).

#### 2.2.4. Paper analysis

The sheets were dried and conditioned for 24 hours at a temperature of 23 °C and a relative humidity of 50%. The physical, mechanical and optical properties of the papers were measured in accordance with the ISO standard methods. The formation was measured with a Micro-Scanner (OpTest Equipment Inc.) which employs a technique based on image analysis by light transmission. The filler content in paper was determined as ash content in accordance with ISO 1762.) Filler retention was calculated by:

$$\text{Filler retention}\,(\%) = \frac{(\text{Filler remained in a sheet, g}) \times 100}{\text{Filler added to a sheet, g}}$$