Effect of Calendering on the Properties of Paper Containing Flexible Calcium Carbonate with a Cellulose Nanofibril Core
Sang Yun Kim, Yung Bum Seo, and Jung Soo Han*

ABSTRACT: Flexible calcium carbonate (FCC) was prepared by attaching a large amount of calcium carbonate to cellulose nanofibrils (CNFs) by an in situ calcium carbonate formation method. FCC normally consists of CNFs and calcium carbonate at a 1:40 ratio by weight. FCC-containing papers resulted in a higher bulk, higher stiffness, and higher tensile strength than a commercialized ground calcium carbonate (GCC)-containing papers at the same ash content. However, there were speculations that calendering on FCC-containing paper might cause a large drop in bulk and no increase in smoothness due to the larger size of the FCC (avg. dia. 20–30 μm) than the GCC (dia. 2 μm). FCC-containing paper was shown to respond to the calendering process very effectively to increase the Bekk smoothness and to maintain high bulk. Furthermore, FCC-containing paper was so effective in increasing smoothness that it might need less calendering pressure to match the smoothness of GCC-containing paper. If so, there could be potential to increase the bulk and stiffness further in FCC-containing papers at the same smoothness as GCC-containing paper by applying reduced calendering pressure.

INTRODUCTION
According to U.S. Energy Information Administration, the pulp and paper is considered to be one of the energy-intensive industries, accounting for approximately 5% of the total industrial sector energy consumption. Even though energy consumption includes all the paper-related sectors such as printing industry, energy savings in papermaking still should be an important issue. High loading of fillers in printing paper may reduce the drying energy and production cost as long as the physical and mechanical properties are within the specification. Replacing wood pulp with inorganic fillers may increase the solid content of the wet web in the wet pressing process, resulting in less use of steam in the drying process and saving expensive wood fiber. However, a high amount of fillers in printing paper usually leads to the production of paper that does not meet specifications due to insufficient tensile strength, low bulk, and low stiffness. To produce highly loaded paper without lowering quality, several methods, such as filler preflocculation, filler lumen loading, colloidulation of fines and fillers, and “superfilling”, which is an in situ calcium carbonate forming method on wood fines, have been introduced and have achieved improvement of fiber bonding properties but have failed to increase paper bulk, which is the volume per unit weight and expressed as cm³/g. Bulk in paper is important to maintain or increase the paper stiffness, which is an essential paper property. In fact, paper stiffness is proportional to the third power of the paper bulk.

Hybrid calcium carbonate (HCC) and flexible calcium carbonate (FCC) were introduced and have shown significant improvement in paper bulk while increasing tensile strength properties. HCC is a large aggregate of both ground calcium carbonate (GCC) and newly formed precipitated calcium carbonate (PCC) created during the in situ calcium carbonate process. HCC is semirigid and seems to be resistant to wet pressing pressure to some extent in the papermaking process. FCC is also deformable to keep the paper surface smooth by conforming to the surface contour of the press nip. Small filler particles that impair hydrogen bonding formation between wood fibers seemed to be attached to the body of the large HCC particles, and the paper tensile strength, thereby, was increased. FCC consists of core cellulose nanofibrils (CNFs) and PCC attached around the nanofibrils. The FCC is large, flexible, and deformable and has 2–5 aspect ratios. When used in papermaking, it gives higher bulk and higher tensile strength than both HCC and GCC. A CNF/PCC composite using ionic polymers was developed and showed improvement in strength and optical properties but could not increase the bulk or stiffness.

In the manufacture of printing paper at the paper mill, surface smoothness is very important, and calendering should be applied...
until at least the low limit of the smoothness specification is reached. Even though FCC-containing paper initially has better smoothness and higher bulk than GCC-containing paper before calendering, we do not know how much the smoothness will be improved by the calendering. In this work, the smoothness development behavior of FCC-containing paper in comparison to GCC-containing paper was investigated. For comparing to GCC, we used two types of GCCs [extraordinarily large size GCC (avg dia. 10 μm, GCC 10 μm) and commercially used GCC (avg dia. 2 μm, GCC 2 μm) for printing paper grade] for demonstrating that the simultaneous improvement of bulk and smoothness of FCC-containing paper is derived from not only their filler size but also their deformable and flexible characteristics. If FCC-containing paper has excellent properties for developing high smoothness in addition to high tensile strength and bulk, the use of FCC in printing paper should be encouraged.

Figure 1. (a) SEM images of the CNF sample and (b) analysis of the morphology of individual fibrils.

Figure 2. Preparation process schematic of the in situ-formed FCC and its filled handsheets. (a) Microscopic images of the CNF and prepared FCC, (b) schematic of the in situ carbonation batch system, and (c) papermaking process and lab calendering [manufactured by PSC (Provider of Solution Completion) Co., Daejun, Republic of Korea].
EXPERIMENTAL SECTION

Preparation of CNFs. Dry lap of hardwood bleached kraft pulp (a mixture of aspen and poplar from Canada) was used for the preparation of the CNFs. We disintegrated this material and refined it with a laboratory valley beater to 150 mL CSF [Canadian standard freeness, Technical Association of the Pulp and Paper Industry (TAPPI) T227 om-99] as a pretreatment. Further mechanical fibrillation was executed by using a Supermasscolloider (Masuko Sangyo Co., Ltd., Japan), which is an ultrafine grinding machine. The gap between the two grinding stones was kept at $-120 \mu m$ from the zero position by controlling the bottom grinding stone after the pulp was loaded. The number of passes and duration of each pass were recorded to evaluate the fibrillation energy. We applied up to 30 passes for the refined hardwood pulps in 2% consistency. The TAPPI has proposed standard terms and their definition for cellulose nanomaterials based on fibril size.\(^1\)\(^9\),\(^2\)\(^0\) They proposed the widths of the nanofibrils and microfibrils to be 5$\text{−}30$ and $10\text{−}100$ nm, respectively. The ISO defines rodlike material as a nanofiber when the two external dimensions are less than 100 nm. We measured the dimensions of the fibrils using a scanning electron microscope (S-4800 model, Hitachi, Japan). To measure the width and length of individually dispersed fibrils, a droplet of diluted fibril suspension (0.001%, w/w) was deposited on a (3-aminopropyl) trimethoxysilane-modified silicon wafer and air-dried according to a previously described method.\(^2\)\(^2\) The dried sample was coated with a platinum layer and analyzed. By measuring at least 300 fibrils using the image analysis program, we found that the average length and width of the fibrils were $5.00 \pm 2.09 \mu m$ and $45.2 \pm 17.1$ nm, respectively (Figure 1). We used those fibrils for the FCC preparation and referred to these preparations as CNFs.

Preparation of FCC. Figure 2a,b shows the schematics of the FCC preparation process. For that, the consistency of the CNF was controlled to be 0.2% at 30 °C. In 1 L of CNF suspension with 2 g of CNF (dry weight), 44.9 g of calcium oxide (Reagent grade, Showa Chemical Co Ltd. Japan) was added to produce 80 g (CNF/CaCO$_3$ = 1:40) of FCC by injecting carbon dioxide into the suspension. The temperature was initially held at 30 °C and increased due to the exothermic reaction to 33–34 °C at the end; this mixture was constantly stirred at 350 rpm. When the pH reached 7.0, we waited 2 more minutes to confirm the stable pH and terminated the reaction. It took approximately 30 min to prepare the FCC. For comparison, two types of commercial GCCs [extraordinarily large size GCC (avg dia. 10 μm, GCC 10 μm) and commercially used GCC (avg dia. 2 μm, GCC 2 μm)] for printing paper grade. Omya, Switzerland) were used to produce GCC-containing papers.

Figure 3. Morphologies of the fillers and the surface of the sheets containing 30% fillers before and after calendering [(a) GCC 2 μm, (b) GCC 10 μm, and (c) FCC] with a 100 kN/m calendering pressure. The papers before calendering were all wet pressed to remove excess water before drying. Physical properties of the GCC- and FCC-containing papers.
Handsheet Preparation and Physical Property Evaluation. To compare the potential of FCC and GCC as a paper filler, we prepared handsheets that consisted of three different amounts of FCC and wood fibers (Figure 2c). The wood fibers were a mixture (80:20) of hardwood bleached kraft pulp (a mixture of aspen and poplar) and softwood bleached kraft pulp (a mixture of hemlock, Douglas fir, and cedar) as the wood fiber furnish, both originating in Canada. These wood pulps were refined together in a valley beater until their freeness reached 500 mL of CSF. They were then mixed with FCCs and GCCs to make handsheets of 80 g/m² basis weight with 20, 30, and 40 wt % ash content (denoted as FCC 20%, FCC 30%, and FCC 40%; GCC 2 μm 20%, GCC 2 μm 30%, and GCC 2 μm 40%; GCC 10 μm 20%, GCC 10 μm 30%, and GCC 10 μm 40%, respectively) according to the TAPPI standard method (T205 sp-95). For the handsheet with 40% ash content for FCC-containing paper, we prepared another type of handsheet by adding 3 wt % cationic starch with 0.037 degrees of substitution, including quaternary ammonium groups (Suncasta 6020, Samyang Korea), based on the dry weight of the furnish for tensile strength supplementation (FCCS 40%). As a retention aid for papermaking, cationic polyacrylamide (MW 5−7 million g/mol, charge density: +5 mequiv/g) from CIBA Specialty Chemical Korea was used (0.1% based on the dry weight of the furnish). Paper testing was executed according to standard methods. The following tests were performed: ash content (TAPPI 413 om-93), bulk (TAPPI T411 om-97), tensile strength (ISO 1924), Bekk smoothness (TAPPI T479 cm-99), and Gurley stiffness (TAPPI T543 om-00).

Calendering. The calendar used in this study was manufactured by PSC Co. in South Korea (Figure 2c), and the calendering load was controlled by air pressure. The calendar rolls had hard nip surfaces. The calendering speed could be controlled from 20 to 200 cm/min, and we used 50 cm/min. We selected calendering pressures of 0, 50, 100, and 200 kN/m and applied the calendering process in a conditioned room (50% RH and 20 °C). The calendering variables, such as temperature, pressure, and fiber furnish, may affect the paper surface properties. However, in this study, to compare the potential of FCC and GCC as a paper filler, other factors were equally fixed.

RESULTS AND DISCUSSION

Morphologies of the Fillers and the Paper Surfaces. The morphologies of the fillers and paper surfaces are shown in Figure 3a−c with the magnification bars. When preparing filler samples for SEM, a drop of filler suspension was placed on the sample holder and was allowed to dry. Therefore, all the particles in the filler suspension, including very small particles, are shown in the micrographs. GCC particles had a large variation in size, and there were many extremely small particles. FCC showed no small particles. The calcium carbonate particles had no capability to make hydrogen bonds between wood fibers and decreased the paper strength. Small particles in the GCC had a large specific surface and could effectively decrease the paper tensile strength. The FCC in the papers might form clusters of fillers between wood fibers, and the clusters of the fillers could be deformed during wet pressing and the calendering process (Figure 3c). For the FCC-containing paper in this study, both FCC and fibers were deformed slightly by the wet pressing process and deformed much by the calendering process. There were clean surface fibers in FCC-containing paper, and they could make hydrogen bonds between clean surface fibers (“FCC after calendering” in Figure 3c). The GCC fillers were located randomly in the GCC-containing papers (Figure 3a,b), and...
there were no clean surface fibers present. The papers containing GCC 2 and 10 μm particles seemed to be deformed not by the wet pressing process but by the calendering process (Figure 3a,b). Those deformations by calendering were not by the GCC but by the fibers. Observation of the paper surfaces indicated that the large FCC inside the paper (sometimes more than 100 times larger than GCC 2 μm) was deformable both in the wet pressing and calendering processes, and the paper containing FCC gave an almost equivalent or smoother surface than the paper containing GCCs by the wet pressing process. However, FCC still gave higher bulk and higher stiffness than the other two GCC papers.

Han et al. (2020) presented a new type of filler, FCC, that simultaneously allowed the paper higher bulk and higher tensile strength than GCC. FCC also resulted better smoothness and much higher stiffness in paper materials before calendering than GCC. They discussed increasing the filler content of the paper to save wood fibers and drying energy and successfully demonstrated promising results.

Figure 4 shows the same trend that Han et al. presented: higher bulk, higher stiffness, and higher breaking length, which is the tensile strength after compensation of the basis weight difference, and better smoothness for the FCC-containing paper compared with GCC-containing paper. The GCC 10 μm-containing papers also gave higher tensile strength, higher bulk, and higher stiffness but much lower smoothness than the GCC 2 μm papers. In commercial printing paper manufacturing, there is a need to have the bulk and stiffness as high as possible, while

Figure 5. Bulk property variations of the papers by the application of calendering at the ash content of 20% (top), 30% (middle), and 40% (bottom).
maintaining the target smoothness and tensile strength. The extra bulk and stiffness could be utilized to reduce the basis weight, to raise the filler content, or to promote product quality as premium quality printing paper. To reach the target smoothness, which is usually a Bekk smoothness of approximately 30–40 s, calendering treatment is essential. Therefore, hard nip calendering was applied in a controlled environment.

**Bulk and Bekk Smoothness.** Calendering in paper manufacturing makes the surface of papers smooth enough to enable high-quality printing and writing. During calendering, the paper thickness structure usually collapses to cause low bulk and low bonding properties, while the paper surface becomes smooth. Figure 5 shows the effects of calendering on the bulk of the papers. The bulk of the papers were all significantly lowered by calendering, while the FCC-containing papers still maintained a much higher bulk than GCC-containing paper at ash contents varying from 20 to 40%. The GCC 10 μm-containing papers still had high bulk over the GCC 2 μm-containing papers. The Bekk smoothness was increased for both the FCC and GCC fillers by calendering, as shown in Figure 6. Before calendering, there was little difference between FCC- and GCC-containing papers, but after calendering, FCC-containing papers developed very high smoothness. To be close to the Bekk smoothness of the GCC-containing paper, FCC-containing papers may need

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**Figure 6.** Bekk smoothness variations of the sample papers by the application of calendering at the ash content of 20% (top), 30% (middle), and 40% (bottom).
less calendering pressure, and less pressure in calendering normally causes less reduction of the bulk and bonding properties. In other words, FCC-containing papers may develop much higher bulk and breaking lengths than GCC-containing papers if we want to equalize the smoothness levels of the FCC-containing papers to those of the GCC-containing papers. The GCC 10 μm-containing papers never reached a Bekk smoothness of 40 s, and it seemed that there was no chance to increase the smoothness using a calendering pressure of less than 200 kN/m. Therefore, the GCC 10 μm cannot be used to produce printing papers, and there was no need to discuss the GCC 10 μm fillers further for the other physical properties in this paper.

**Stiffness and Breaking Length.** The breaking lengths of the FCC-containing papers were higher than those of the GCC 2 μm-containing paper, as shown in Figure 7, even though the bulk of the FCC-containing papers was much higher than those of the GCC-containing papers (Figure 5) at various calendering pressures. For the FCC-containing papers with 40% filler, the addition of starch (FCCS 40%) increased the breaking length equivalent to those of the GCC 2 μm-containing paper with 30% filler. The reason why the FCC-containing papers had a higher breaking length than the GCC 2 μm-containing papers was because there was much less presence of small particles in FCC

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**Figure 7.** Breaking length variations of the sample papers by applying calendering at the ash content of 20% (top), 30% (middle), and 40% (bottom). FCCS 40% was the paper containing 40% FCC with 3% cationic starch.
that disturbed the formation of hydrogen bonding between wood fibers.

High bulk should cause high stiffness. In fact, high bulk resulted in high stiffness, as presented in Figure 8. Decreasing the bulk by calendering caused a stiffness decrease. If a target smoothness value of the paper is a main controlling factor in the manufacture of printing paper, we may need to apply less calendering pressure to FCC-containing papers because at the same calendering pressure, FCC-containing papers gave higher Bekk smoothness than the GCC-containing papers (Figure 6). Less calendering pressure may reduce the decrease of the paper bulk and cause the stiffness to increase. No change in stiffness was shown for the papers containing 40% FCC with and without starch addition.

When bulk properties were plotted against the Bekk smoothness, two different fillers gave two different groups of curves, as shown in Figure 9a. It appears that the type of fillers made clear differences of the bulk at the same Bekk smoothness values (Figure 9a). The FCC-containing papers gave a much higher bulk. The curves of breaking length versus Bekk smoothness showed that the FCC-containing paper gave higher breaking length than GCC-containing papers at the same ash content and at the same Bekk smoothness (Figure 9b). The “FCCS 40%”, which was the case of “FCC 40%” with 

(Figure 3c) that disturbed the formation of hydrogen bonding between wood fibers.

Figure 8. Stiffness variations of the sample papers by the application of calendering at the ash content of 20% (top), 30% (middle), and 40% (bottom). FCCS 40% was the paper containing 40% FCC with 3% cationic starch.
addition of starch, gave as much breaking length as the “GCC 30%” case (Figure 9b) while maintaining a high bulk (Figure 9a). Therefore, it may be said that the FCC-containing paper showed higher bulk, higher tensile strength, higher Bekk smoothness, and higher stiffness than the GCC-containing paper both before and after calendering when compared at the same ash contents.

**Saving Wood Fibers.** Improvement of physical properties by using FCC fillers should be materialized into economic and environmental benefits. High loading of inorganic fillers in paper may save wood fiber and production costs. Figure 10 shows the comparison of four different cases of using fillers (GCC 2 μm 30%, FCC 30%, FCC 40%, and FCCS 40%), where the physical properties of the papers were interpolated from Figure 9 and the stiffness versus Bekk smoothness graph in Figure S1 at the same Bekk smoothness values (30 and 40 s) with no calendering case of the papers. From the figures, it was found that there were almost no changes in the property patterns among three different smoothness levels. In any case, the paper with FCCS 40% could result in a 10% wood fiber savings when compared to the paper with GCC 2 μm 30% with much higher stiffness and bulk as bonus. The addition of 3% starch to the fiber furnishes for the case of FCCS 40% only caused an increase in breaking length for the FCC 40% case. Less use of wood fibers will lead to protection of the forest and reduce paper production costs.

**CONCLUSIONS**

FCC was prepared by attaching a large amount of calcium carbonate to CNFs, and these nanofibrils were then used as the core of FCCs using an in situ calcium carbonate formation method. The properties of the FCC were compared to those of the GCC in papermaking with respect to its superiority in terms of the paper physical properties. FCC paper developed higher bulk, higher smoothness, and higher stiffness before and after calendering and showed superiority in developing smoothness over GCC in response to the calendering. Therefore, FCC-containing paper needed less calendering pressure to achieve a smoothness equal to that of the GCC-containing paper. Large size GCC (approximately 10 μm in average dia.) did not develop the smoothness enough for the printing paper by calendering, even though the large size GCC was helpful in increasing the bulk and tensile strength. Increasing the filler content and saving
wood fibers by about 10% in printing paper manufacturing was found to be feasible when replacing GCC to FCC, while still maintaining essential paper physical properties. The FCC-containing paper was turned out to respond quite well to the calendering pressure with respect to developing Bekk smoothness.

**Figure 10.** Property ratios of the sample papers with/without calendering (a) and with calendering at a Bekk smoothness of 30 (b) and 40 s (c). The properties of GCC 30%-containing papers were calculated as 100%.

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**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acsomega.2c04967](https://pubs.acs.org/doi/10.1021/acsomega.2c04967).

The graph of the stiffness versus Bekk smoothness of papers ([PDF](https://pubs.acs.org/doi/10.1021/acsomega.2c04967)).
AUTHOR INFORMATION

Corresponding Author

Jung Soo Han — Institute of Agricultural Science, Chungnam National University, Daejeon, Gung-Dong 305-764, Republic of Korea; orcid.org/0000-0002-8275-138X; Email: han1606@cnu.ac.kr

Authors

Sang Yun Kim — Department of Biobased Materials, Chungnam National University, Daejeon, Gung-Dong 305-764, R.O. Korea

Yung Bum Seo — Department of Biobased Materials, Chungnam National University, Daejeon, Gung-Dong 305-764, R.O. Korea

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c04967

Notes

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