Investigation of the Mixed Refining of a Novel Fly Ash-based Calcium Silicate Filler with Fiber

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In this paper, the mixed refining of fiber and a novel fly ash-based calcium-silicate (FACS) filler is proposed as a new filler application method, as it has some advantages over the traditional filling method. Paper produced using this filler application technique exhibits improved strength and optical properties but reduced bulk. SEM images were obtained to show the FACS filler-fiber composite structure that formed during the mixed refining process. Two models were proposed to describe the mechanism by which the mixed refining process improved the paper properties. Mixed refining can decrease the size of FACS particles, especially if the filler/fiber ratio is low. It was suggested that handsheets filled with small FACS particles had low bulk, which was beneficial for increasing the interfiber H-bonding. Decreasing the filler/fiber ratio improved the paper strength and optical properties at the expense of some bulk, a loss which varied depending on filler content.

Keywords: Paper filler; Fly ash; Calcium silicate; Mixed refining; Tensile; Bulk; Optical properties

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INTRODUCTION

Filler is the second most used raw material in some grades of paper. Fillers increase the opacity and brightness of paper, as well as improve its formation and printing properties (Chauhan *et al*. 2012). The energy consumption of the papermaking process can also be reduced by the addition of a filler, since fillers can improve the capacity for water removal during the pressing and drying stages (Allan *et al*. 1997; Kenaga *et al*. 1982; Liimatainen *et al*. 2006). Furthermore, the addition of a filler might reduce the production costs, because mineral fillers are often cheaper than wood fibers (Dong *et al*. 2008). However, many common fillers can decrease paper strength, which places limits on the proportion of filler that can be incorporated into paper.

Certain filler parameters, such as density and particle shape, can greatly impact paper strength (Bown 1998). High-density fillers such as $BaSO_4$ have a smaller volume per unit weight and, therefore, cause less debonding per unit weight than would a less dense filler. The silicate nano-fiber (SNF) is a new type of silicate filler with a fibrous shape that could replace the TiO_2 as a paper filler (Mathur 2004). Paper filled with SNF has good optical and strength properties. In one filling method, called interlay filler adding technology, the filler is added between two layers of the wet paper web, which results in a relatively small decrease in paper tear strength and good filler retention (Cui and Han 2011).

Fly ash is a by-product of coal-fired thermal power plants. In 2012, the emission of fly ash in Inner Mongolia alone exceeded 12 million tons, and the number is increasing annually by 20% (Sun *et al*. 2012). This large amount of fly ash causes serious air pollution and increases the danger of groundwater contamination. Therefore, there are strong environmental, economical, and social incentives for finding a suitable application for fly-ash. Previous studies have demonstrated that calcium silicate material made from fly ash, referred to as fly ash-based calcium silicate (FACS), could be used as paper filler. FACS has a highly porous structure, high brightness (91% ISO), and a high specific surface area (121 m^2/g) (Song *et al*. 2012; Wu *et al*. 2012). Because of its large particle size and porous honeycomb structure, paper loaded with FACS has higher bulk and strength than similar paper loaded with precipitated calcium carbonate (PCC) (Zhang *et al*. 2013).

In this paper, a novel method of filler application is proposed, which includes the refining of the pulp suspension that contains the FACS filler to improve paper properties, and the results were compared with those obtained by the traditional filling method.

EXPERIMENTAL

Materials

The FACS filler, which was provided by a coal-fired power plant, had a particle size of 23 μm, a true density of 1.3 to 1.4 g/cm^3, a specific surface area of 121 m^2/g, and an ISO brightness of 91%. The fiber furnish used in this study was a blend of 20% bleached softwood kraft pulp and 80% bleached hardwood kraft pulp, provided by a pulp mill in Fujian, China. The average length of hardwood fibers and softwood fibers were 824 μm and 1897 μm, respectively. The brightness of paper made from hardwood fibers and softwood fibers were 79 ISO% and 82 ISO%, respectively. Cationic polyacrylamide (CPAM), used as a retention agent, was supplied by the Nalco Chemical Company, Nanjing, China.

Methods

Mixed refining of pulp and filler

The FACS filler suspension (15 wt %) was added to a pulp slurry containing 30 g of oven-dried pulp. The blend of pulp and FACS filler, with the filler/fiber ratio ranging from 0.15 to 0.6 (based on oven-dry materials), was refined in the PFI mill after 5000 revolutions at the consistency of 10 wt%. In order to investigate the effect of filler/fiber ratio on paper properties, the ratios of filler/fiber were fixed at 0.15, 0.3, 0.4, and 0.5, respectively. For the traditional filling method, only fiber was refined using the same number of revolutions, and then the filler was added to the refined pulp in a filler/fiber ratio ranging from 0.1 to 0.5. The freeness of the refined pulp without filler was 30° SR.

Handsheet preparation

Handsheets of 70 g/m^2 were prepared using a circular laboratory sheet former. The paper furnish was diluted to a concentration of 0.375 wt%, and then the cationic retention agent (CPAM) was added in dosages between 0% and 0.07% based on the oven-dry fiber amount. Sheets with different filler contents were formed from each filler/fiber suspension by changing the amount of CPAM. The filler content was kept under 30%. The wet sheets were pressed according to the TAPPI test method T 205 sp-95 and then dried at 105±2 °C for 9 min. In preparation for testing, the handsheets were stored for 24 h at 25 °C and at 50% relative humidity.

Test of paper properties

The paper properties, including bulk, tensile index, brightness, and opacity, were tested in accordance with the relevant TAPPI test methods. The morphology of filled paper was observed by means of S-4800 scanning electron microscopy (SEM). The filler content was determined after the paper samples were ashed at 525 °C in accordance with TAPPI test method T211 om-93.

RESULTS AND DISCUSSION

Comparison between Mixed Refining and Traditional Filling Methods

Paper properties

The mixed refining of FACS with pulp was compared with the traditional filling method at 5000 revolutions. The paper filler content was changed by increasing the amount of filler added into the furnish. The percentages of filler added, with respect to oven-dried pulp, were 15%, 30%, 40%, 50%, and 60% for the mixed refining, and 10%, 20%, 30%, 40%, and 50% for the traditional filling method. The handsheet properties are shown in Figs. 1 through 4.

As illustrated in Fig. 1, the bulk of handsheets made after mixed refining was lower when compared to those obtained by the traditional filling method, and the difference between these two filling methods decreased as the filler content increased. After the mixed refining procedure, the resultant FACS particles were smaller relative to those of the traditional filling method. This could have been what was responsible for the lower bulk of the paper made using the mixed refining method.

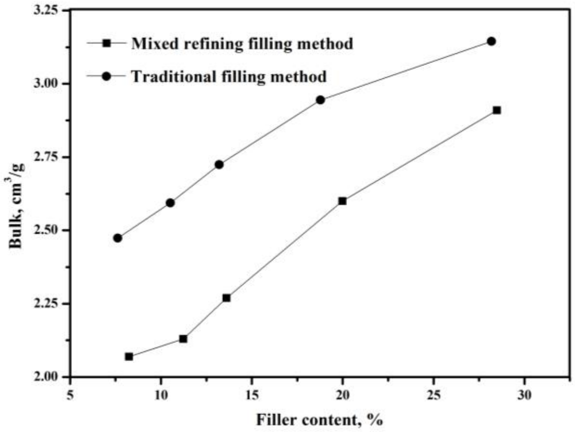

Fig. 1. The bulk of handsheets, as filled by the two methods

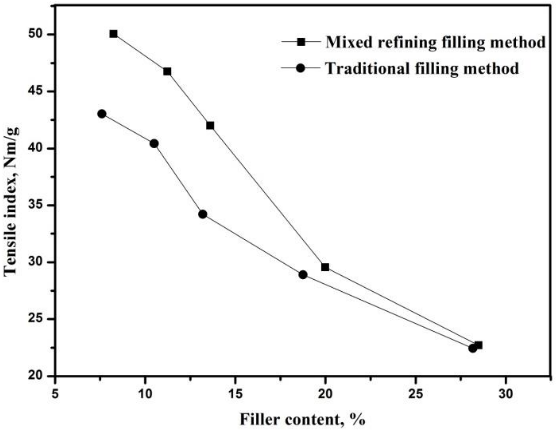

Fig. 2. The tensile strength of handsheets, as filled by the two methods

When the FACS filler was used, the mixed refining resulted in improved handsheet strength (Fig. 2), even though the filler particle size was decreased. There was no significant difference in paper strength between these two filling methods in the high filler content conditions (above 20%). It is widely known that fillers with small particle size have greater negative effects on paper strength (Li *et al*. 2002). However, the lower bulk of the paper made by mixed refining typically provides for more hydrogen bonding, and thus improves paper tensile strength, which can partly explain the improvement in paper strength that was observed.

The optical properties of paper can be improved by the addition of a filler, and this effect can be enhanced by using a filler with a small particle size (Kumar *et al*. 2009). As shown in Figs. 3 and 4, the brightness and opacity of FACS-filled paper can be markedly improved by mixed refining, a phenomenon that can be attributed to the decrease in filler particle size that occurs during mixed refining. Therefore, mixed refining can provide some benefits in terms of paper strength and optical properties, which may bring some potential applications for paper grades with filler contents below 20%.

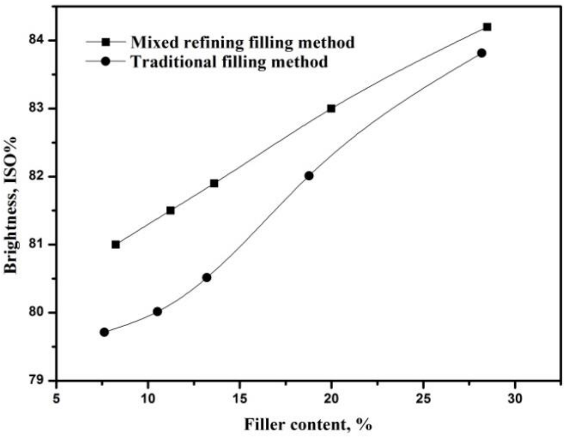

Fig. 3. The brightness of handsheets, as filled by the two methods

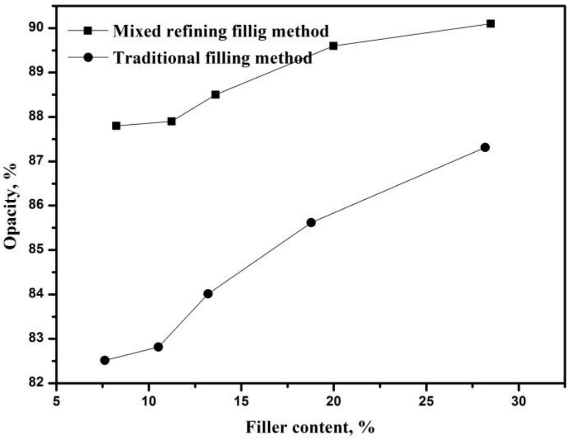

Fig. 4. The opacity of handsheets, as filled by the two methods

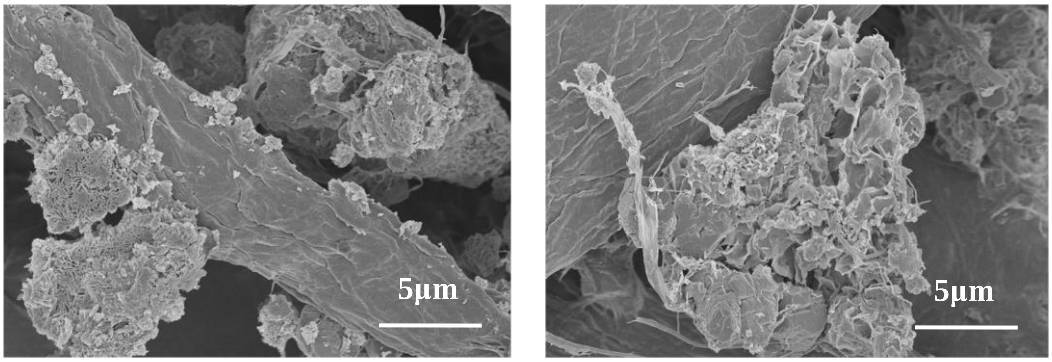

Fig. 5. SEM images of handsheets made using traditional filling method

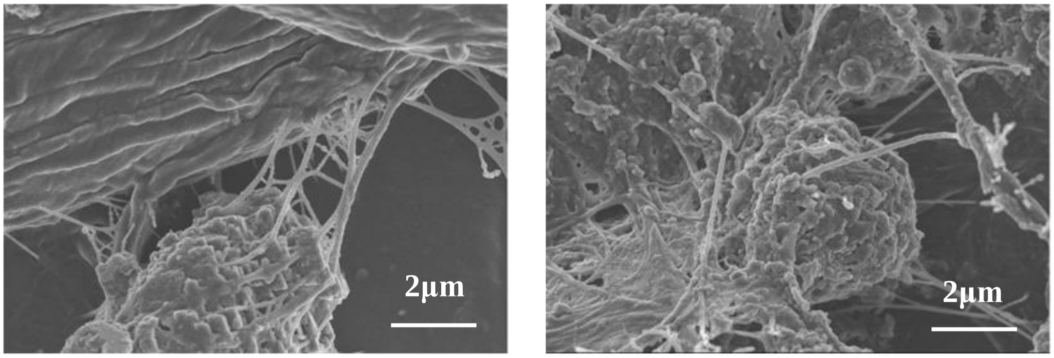

Fig. 6. SEM images of handsheets made using mixed-refined furnish

The highly porous structure of the FACS provides it with a high specific surface area and leads to particle flocculation. The original FACS particle size was 23 μm. Agglomerations of small particles were destroyed by the refining, and the FACS particles in the refined furnish got smaller. The composite structures of FACS and fiber found in the paper subjected to mixed refining were different from those produced by the traditional filler method, as illustrated in Figs. 5 and 6. The FACS particles were entwined by the microfibers generated in the fibrillation and had adhered to the fibers. This connection between filler and fiber may have helped to alleviate the negative effects of filler on paper strength.

Mechanism model

Two models were proposed to describe the mechanism behind the improvement of paper properties by mixed refining. As shown in Fig. 7, in the traditional filling method, the FACS filler can be seen to exist in the voids or between the fibers. In contrast, in the mixed refining, the inter-fiber bonding might be formed through microfibers, which package the filler particles and mitigate the detrimental effects of the FACS on fiber bonding. Generally, the addition of an inorganic filler into paper can block the hydrogen bonds between the fibers and diminish the paper strength (Fatehi *et al*. 2010). However, the creation of the filler-fiber composite structure during mixed refining could reduce the negative debonding effect of the FACS filler. The mixed refining filling method was beneficial for improving paper strength, as shown in Fig. 2.

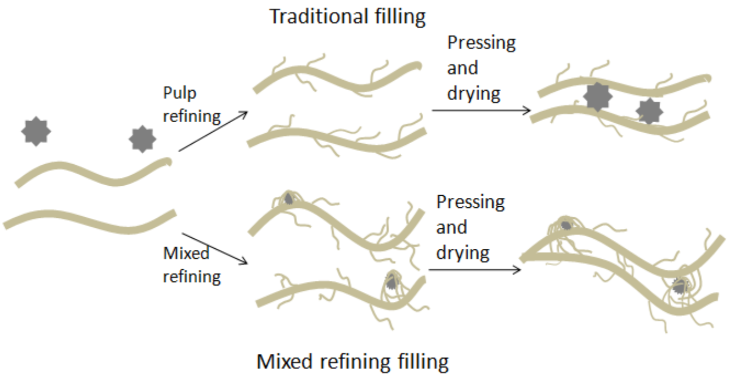

Fig. 7. Illustration of composite structure formation process

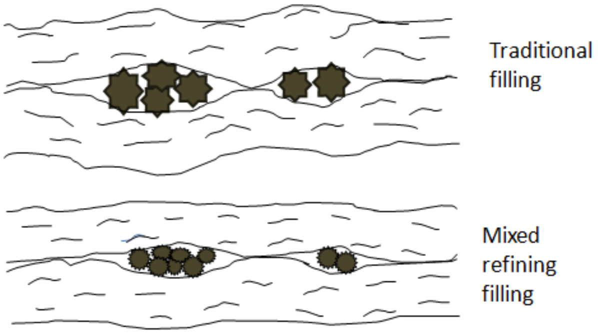

Fig. 8. Packing of FACS particles in handsheets

The model represented in Fig. 8 illustrates the packing of FACS particles in the handsheets. Compared with the traditional filling method, the FACS filler, after undergoing the mixed refining process, exhibited particles of smaller size and which were more tightly packed. The small FACS filler particles decreased the paper bulk and promoted interfiber bonding. The tight aggregates of FACS particles were able to decrease the number of particles, which is beneficial for mitigating the negative effects on paper strength. At the same time, the decline in the size of the filler particles increased the light scattering coefficients of the FACS filler. The above analyses could explain the enhanced paper properties achieved by using the mixed refining filling method, as well as the decrease in paper bulk (Figs. 1 through 4).

Effect of the Ratio of Filler to Fiber on Paper Properties

The amount of pulp in the suspension remained constant at 30 g. At a higher ratio of filler to fiber, the total amount of solids in the pulp-fiber suspension was greater, and consequently, less refining power was delivered *per* unit weight of pulp and filler. The lower refining power caused a smaller reduction in filler particle size and less refining of fibers. The different refining powers at various filler/fiber ratios resulted in different handsheet properties for these various ratios.

When comparing the handsheets of equal filler content, those prepared from suspensions refined at higher filler/fiber content ratios had higher bulk, as shown in Fig. 9. Furthermore, suspensions refined at higher filler/fiber content ratios yielded handsheets with lower tensile index, and lower brightness and opacity, as illustrated in Figs. 10 through 12.

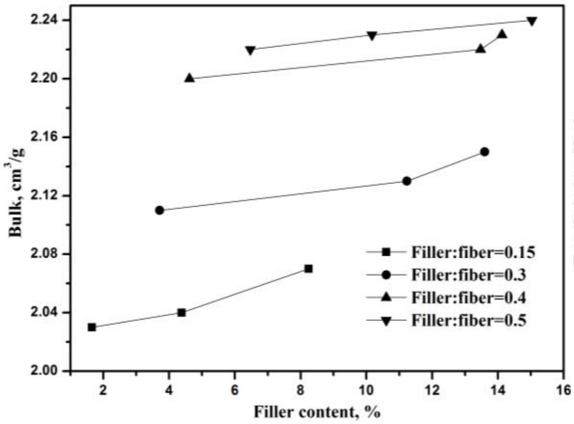

Fig. 9. Effect of ratio of filler to fiber on handsheet bulk (5000 revolutions)

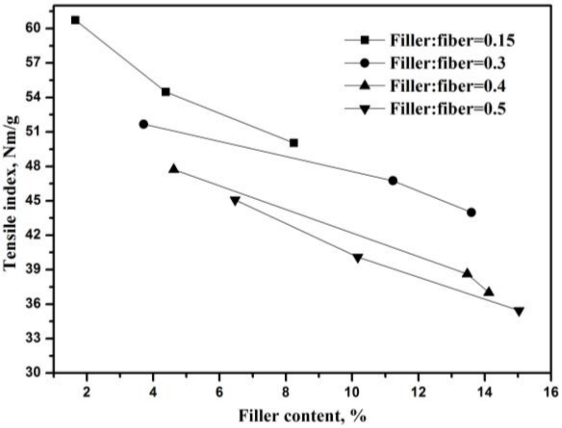

Fig. 10. Effect of ratio of filler to fiber on handsheet strength (5000 revolutions)

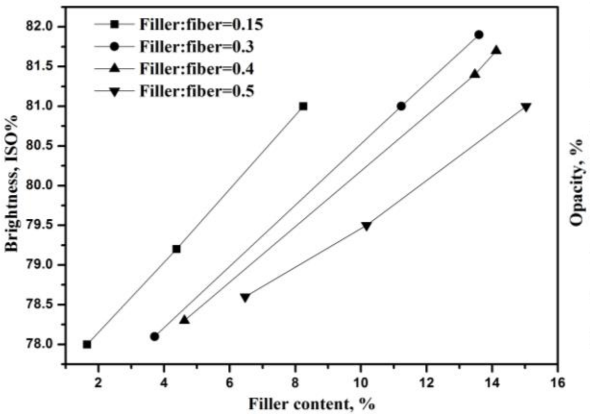

Fig. 11. Effect of ratio of filler to fiber on paper brightness (5000 revolutions)

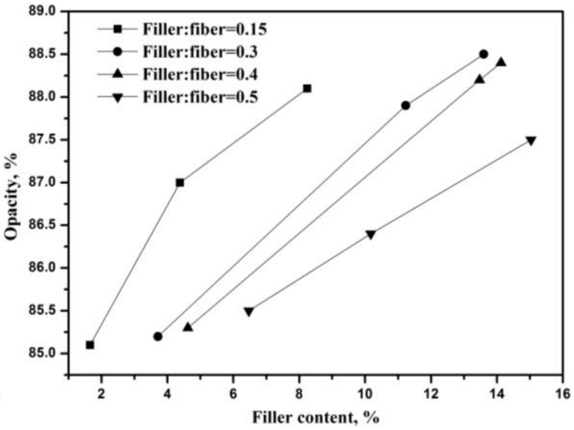

Fig. 12. Effect of ratio of filler to fiber on paper opacity (5000 revolutions)

Decreasing the ratio of filler to fiber led to a reduction in FACS particle size. Smaller particles are able to open smaller interfiber spaces within the paper (Hubbe and Gill 2004), which contributes to the reduced paper bulk. The light scattering coefficient of the FACS filler was increased and more filler-air-fiber interfaces were formed as the particle size decreased, resulting in the improved brightness and opacity. In general, smaller particle size has a more detrimental effect on the paper tensile index (Hubbe and Gill 2004). However, in the case of mixed refining, the smaller size of the FACS particles had a less negative effect. This observation might be rationalized in three ways: (1) the smaller particles were packed more tightly, causing fewer defects and voids in paper and preserving more interfiber bonding (Velho 2002); (2) the smaller FACS particles might have been more likely to form the tightly composite structure; and (3) the silanol in the FACS fillers might have produced additional hydrogen bonds.

The primary component of FACS is hydrated calcium silicate, and silanol bonds can be formed when silicate filler are used (Mathur 2004). For this reason, hydrated calcium silicate was used as a reinforcement filler in silicone rubber (Peng *et al*. 2010). FACS with smaller particle sizes should have more silanol groups and more possibilities to form silanol-originated hydrogen bonds, resulting in a higher tensile index than would occur for larger-particle FACS fillers. Alternatively, as mentioned earlier, the effect might be attributed to the enfolding and entangling of the filler particles with cellulosic fibrils.

CONCLUSIONS

In this work, a novel filler application method in papermaking, *i.e.*, the mixed refining of filler and fiber, was proposed. The following conclusions were reached:

1. Compared with the traditional filling method, mixed refining can improve the tensile strength, brightness, and opacity of FACS-filled paper, although it decreases the paper bulk slightly.
2. The composite structures of the FACS filler and fiber could be found in the paper that had been subjected to mixed refining, and did not exist in paper made by the traditional filler-application method. Based on these findings, two possible mechanisms were proposed to explain the improvements in paper properties that occurred during mixed refining, *i.e.*, the fibrillated fiber-FACS composite structure and the improvement of the packing ability of FACS particles.
3. The filler/fiber ratio can influence the paper properties during mixed refining. Decreasing the filler/fiber ratio during mixed refining proved beneficial for improving the strength and optical properties of the paper, although at the expense of some sheet bulk loss.

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