Using a Novel Fly Ash Based Calcium Silicate as a Potential Paper Filler

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A novel calcium silicate filler can be made from fly ash. This new filler, known as fly ash based calcium silicate (FACS), has a highly porous surface structure, high brightness (91% ISO), low bulk density (0.31 g/cm^3), and high specific surface area (121 m^2/g). In this paper, its potential application as a paper filler was studied and its effect on drainage, retention, and paper properties was investigated. The results from dynamic drainage tests showed that FACS had similar drainage and retention behaviors to the conventional precipitated calcium carbonate (PCC). Physical tests indicated that FACS-filled paper had higher tensile, burst, and tear indices, but lower brightness and opacity than those loaded with PCC. A more important finding was that the bulk of paper can be increased by 56.4% with 20% FACS content in paper relative to the control (no filler addition).

Keywords: Paper filler; Calcium silicate; Fly ash; Bulk; Tensile; Retention; Drainage

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INTRODUCTION

Fly ash, a solid waste, is the combustion residue from coal-fired power (thermal power) plants. Its brightness is normally below 30% ISO, (Sinha 2008; Fan and Qian 2012) and its color can range from gray to black. Fly ash contains 35% to 70% SiO_2, 15% to 30% Al_2O_3, 1% to 10% CaO, 5% to 10% Fe_2O_3, 1% to 2% TiO_2, and small amounts of other oxides such as MgO, Na_2O, SO_3, and P_2O_5 (Sinha 2008). Its composition depends on the type of coal used and the process of combustion. There were more than 1400 coal-fired power plants in China as of 2010, which generated about 480 million tones of fly ash (Song *et al.* 2012). Large amounts of fly ash are disposed at landfills near power plants, resulting in environmental concerns. Therefore, the value-added utilization of fly ash has become increasingly important economically, environmentally, and socially. The potential applications of fly ash have been reported in several publications, which include the production of construction materials, road pavement, agriculture, and as sorbent materials (Ferreira *et al.* 2003; Cao *et al.* 2008).

In the modern papermaking industry, filler is the second most consumed raw material in printing/writing grade papers. Since inorganic fillers are usually cheaper than pulp fibers, substituting some fiber with mineral filler is one of the most economical and efficient ways to reduce the cost of paper products (Dong *et al.* 2008; Chauhan *et al.* 2011). Additionally, some paper properties, such as brightness, opacity, printability, and dimensional stability, can be improved by the addition of mineral filler in the papermaking process (Shen *et al.* 2011a,b). However, filler loading weakens paper strength due to the decrease of inter-fiber bonding. Additionally, some wet-end properties, such as drainage and retention, need to be considered when various fillers are used (Chen *et al.* 2011).

Limited results on fly ash-based paper filler have been reported in the literature. Work done by Sinha (2008), suggested that paper loaded with fly ash with a mean particle size of 19 μm yielded higher printing opacity and tear factor. Other properties such as burst index, tensile index, and smoothness had little deviation from comparison with the results of kaolin-clay as the filler. However, the brightness of paper decreased substantially when the fly ash content in paper was higher than 10%. Recent results by Fan and Qian (2012) indicated that when combining screening, floatation, and used together with calcium carbonate, the brightness of the fly ash filler and the resultant paper sheet can be improved to some extent. However, brightness of fly ash remains the key barrier for its application in fine paper.

A process allowing production of high brightness calcium silicate from fly ash was developed (Zhang *et al.* 2008; Song *et al.* 2012). This so-called fly ash based calcium silicate (FACS), can overcome the low brightness of fly ash. In this study, as part of our continuing effort in exploring the potential of FACS as paper filler, we particularly focus on the effect of FACS loading on drainage, retention, and paper properties, as these parameters are critical to the papermaking process and resulting paper properties. The results were compared with those obtained using PCC (Precipitated Calcium Carbonate) as paper filler.

EXPERIMENTAL

Materials

The fiber furnish used in this study was a blend of 25% commercial bleached softwood kraft pulp and 75% bleached hardwood kraft pulp. The freeness of the pulp was 500 mL. The FACS filler was supplied by a coal-fired power (thermal power) plant in China. Its main composition was calcium silicate. The PCC filler (Scalenohedral Albacar HO) was supplied by Specialty Minerals, Inc. Cationic retention aid (CPAM) Percol 182 was provided by Ciba.

Methods

Filler characterization

The particle size and size distribution of filler were measured using a Malvern Mastersizer 2000 particle size analyzer. The brightness of the fillers was tested following TAPPI method T 534 pm-92. The pH of the filler was tested according to the national standard of China of GB/T 19281-2003. Filler specific surface area was determined using the BET method and nitrogen adsorption. Surface morphology of the samples was characterized with a JEOL JSM-6400 Scanning Electron Microscope.

Retention test

A Dynamic Drainage Jar (DDJ) device was used to evaluate the filler retention performance, including first pass retention (FPR), and first pass ash retention (FPAR) (Zhang *et al.* 2007). Four-hundred grams of 0.5% pulp suspension was mixed with 5 g of

10% filler slurry, and the mixture was then diluted to 500 g with water. The furnish was put into the DDJ, which was set at 750 rpm stirring speed for 1 min. Subsequently, 0.05% CPAM was added. Ten seconds later, the first 100 mL of filtrate was collected and then filtered using pre-dried and weighed ashless filter papers. The residues were dried at 105 ^{o}C and reweighed to determine the solids content. The filler content was analyzed by ash content in the paper sample according to TAPPI Method T211.

The FPR and FPAR were calculated according to the following equations (Zhang *et al.* 2009):

$$\text{FPR}(\%) = \frac{\text{Consistency of Stock} - \text{Consistency of DDJ Filtrate}}{\text{Consistency of Stock}} \times 100 \quad (1)$$

$$\text{FPAR}(\%) = \frac{\text{Fillers in Stock}(\%) - \text{Fillers in DDJ Filtrate}(\%)}{\text{Fillers in Stock}(\%)} \times 100 \quad (2)$$

Drainage test

The drainage performance of pulp added with filler was determined with a Mütek DFR-05 apparatus. Six-hundred grams of 0.5% pulp suspension was mixed with 25% filler (based on oven dried fiber), and then was diluted to 1000 g with tap water. The furnish was then put into the stirring chamber and was homogenized with a time interval of 10 sec, at a stirrer speed of 700 rpm. Then CPAM was added into the suspension, and the stirrer was run for another 10 sec at 800 rpm to simulate paper machine speeds below 1000 m/min.

Handsheet preparation and testing

Handsheets of 60 g/m^2 were prepared using a laboratory sheet former. The retention aid CPAM was added into fiber furnish at a dosage of 0.05 wt% based on the oven-dry pulp amount. The filler content of FACS- and PCC-filled paper was kept around 13 and 20 wt% based on oven-dry pulp amount. The wet sheets were pressed according to the TAPPI test method T 205 sp-95 and then air dried at 25.0 °C and 50% relative humidity for 24 h. The porosity was measured according to TAPPI test Method T 460 om-96. Other physical properties of handsheets were tested in accordance with TAPPI test Method T220. The filler content was analyzed following TAPPI test Method T211 om-93.

RESULTS AND DISCUSSION

Filler Characteristics

Synthesized fillers, such as PCC have well-defined sizes and shapes (Mueller *et al.* 2006) The comparison of properties between FACS and PCC are listed in Table 1 (particle characteristics) and Fig. 1 (particle size distribution). FACS filler was found to have a larger particle size of 27.6 μm but similar particle size distribution compared to the PCC. The bulk density of FACS was lower than that of PCC. The large particle size, low bulk density, and narrow particle size distribution can increase the bulk of paper by decreasing the particle packing ability; however, the paper bonding-depended strength properties may be negatively affected.

Evidently, its high specific surface area (from BET results) was another distinction of FACS filler. The higher specific surface area is conducive to higher light scattering efficiency but may disrupt the fiber-fiber bonding and increase the requirement of sizing agent (McLain and Ingle 2009). The brightness of FACS was about five points lower than that of PCC.

Table 1. Characteristics of FACS and PCC

Characteristics	FACS	PCC
Average particle size, μm	27.6	2.7
Particle size distribution*	1.36	1.29
Bulk density, g/cm^3	0.31	0.52
Specific surface area , m^2/g	121	11.6
Brightness, %ISO	91.5	96.3
pH	9.7	9.7
Ignition loss, % (525 ℃)	10.17	0

*Particle size distribution = (d_{90}-$d_{10)}$/d_{50}. The narrower the distribution, the smaller the PSD.

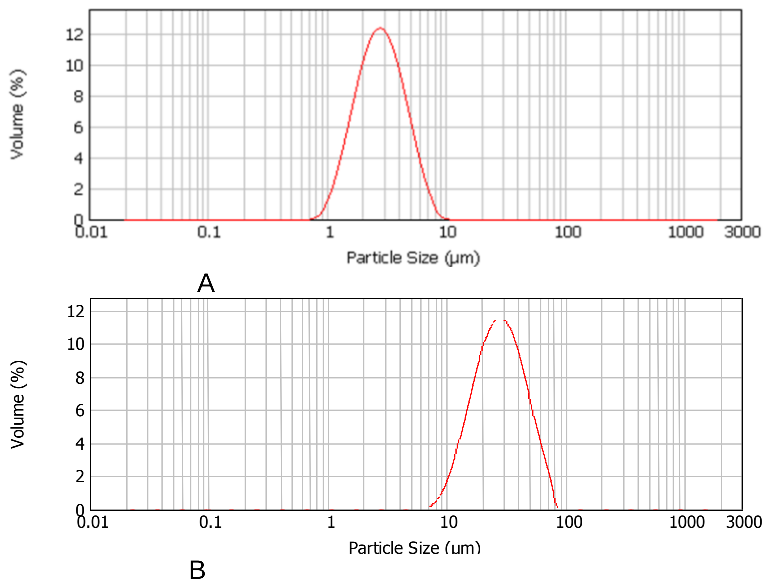

Fig. 1. Particle size distribution of PCC (A) and FACS (B) fillers

The morphological properties of PCC and FACS fillers are shown in Fig. 2. Both fillers exhibited aggregated morphology. PCC exhibited clusters (rosettes) of triangular-shaped crystals. In comparison, there were two types of shapes in FACS filler: needle-like and aggregated particles with wrinkly porous surfaces. Air voids always exist in aggregated fillers. Some paper properties can be affected by the air voids, such as bulk and opacity (McLain and Ingle 2009).

Dynamic Retention and Drainage

Cationic copolymers of acrylamide, *i.e.* CPAM, are common and effective retention aids for improving filler and fines retention (Cheng 2009; Krochak *et al.* 2012; Hubbe *et al.* 2009). As shown in Fig. 3, the FPR and FPAR of FACS and PCC filler were increased when CPAM was incorporated. The results of the two filler retention were similar. In the absence of CPAM, the FACS retention was slightly better than the PCC retention under otherwise the same conditions.

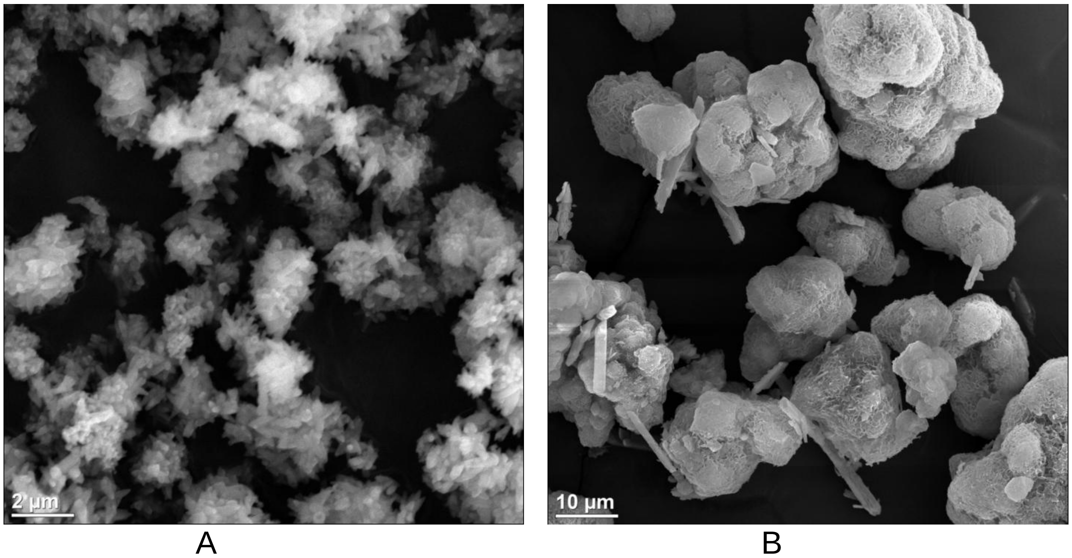

Fig. 2. SEM images of PCC (A) and FACS (B)

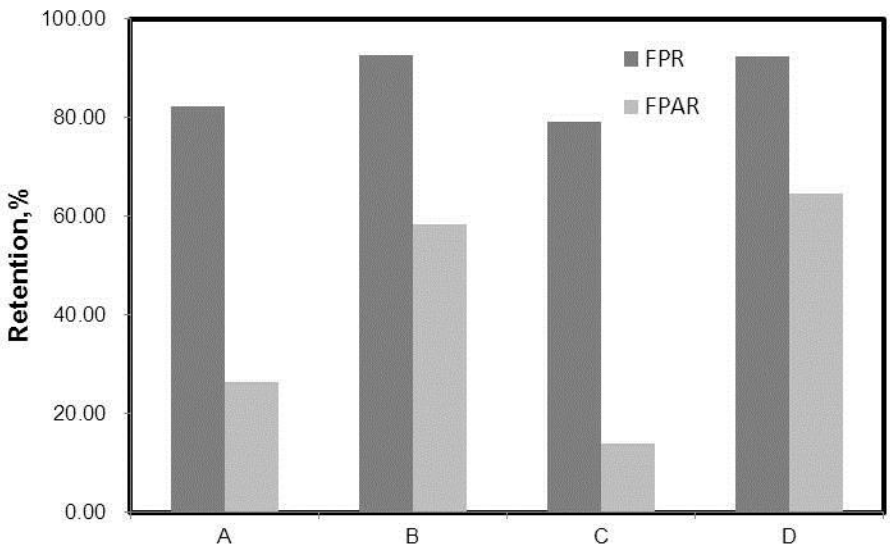

Fig. 3. The first pass retention (FPR) and first pass ash retention (FPAR) of FACS and PCC
A. FACS, without CPAM; B. FACS with CPAM; C. PCC, without CPAM; D. PCC, with CPAM
(DDJ test conditions: CPAM 0.05%, speed 750 r/min, filler addition 25%)

Particles with high specific area may help improve filler retention due to their high adsorption on fines and fibers. Additionally, filler with large particle size often exhibits a higher retention (Cheng 2009). The slightly higher filler retention of FACS may be attributed to these aspects when there is no retention aid in the system. Bridging is the most common mechanism when CPAM is adopted as retention aid (Doiron and Gess 1998). It is especially more effective for fillers with small particle size (Cheng 2009).

The drainage results are shown in Fig. 4. It can be found that the FACS and PCC had similar drainage rate, although the initial FACS drainage rate was higher than that of the PCC.

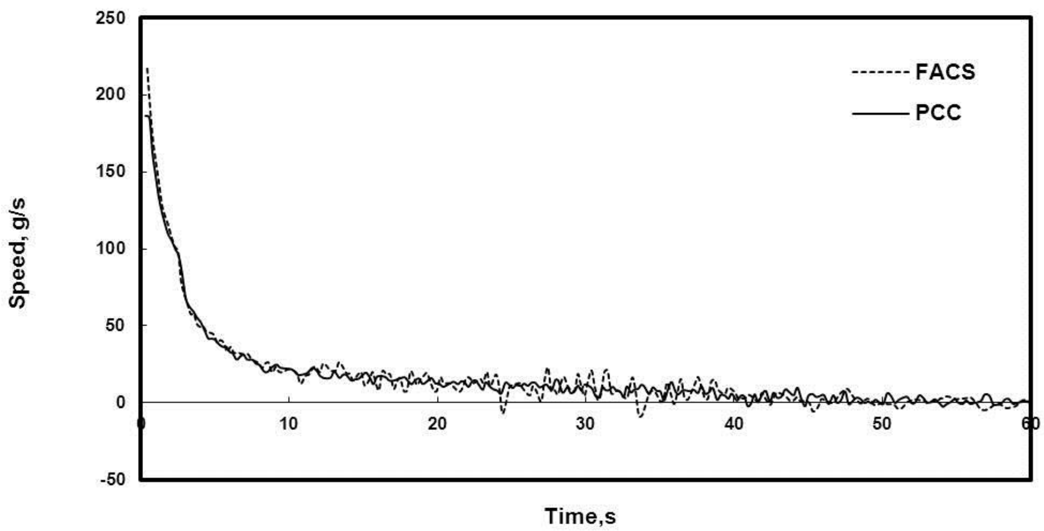

Fig. 4. Drainage rates of FACS and PCC (25% filler addition, 0.05% CPAM, test speed: 800 rpm)

Filler Distribution

Shown in Fig. 5 are the filler distribution results of PCC and FACS on the paper surface. It is evident that the FACS filler had larger particles compared to the PCC filler. The aggregate structure of the FACS filler can be readily seen. In addition, PCC particles with small particle size were readily adsorbed around fibers.

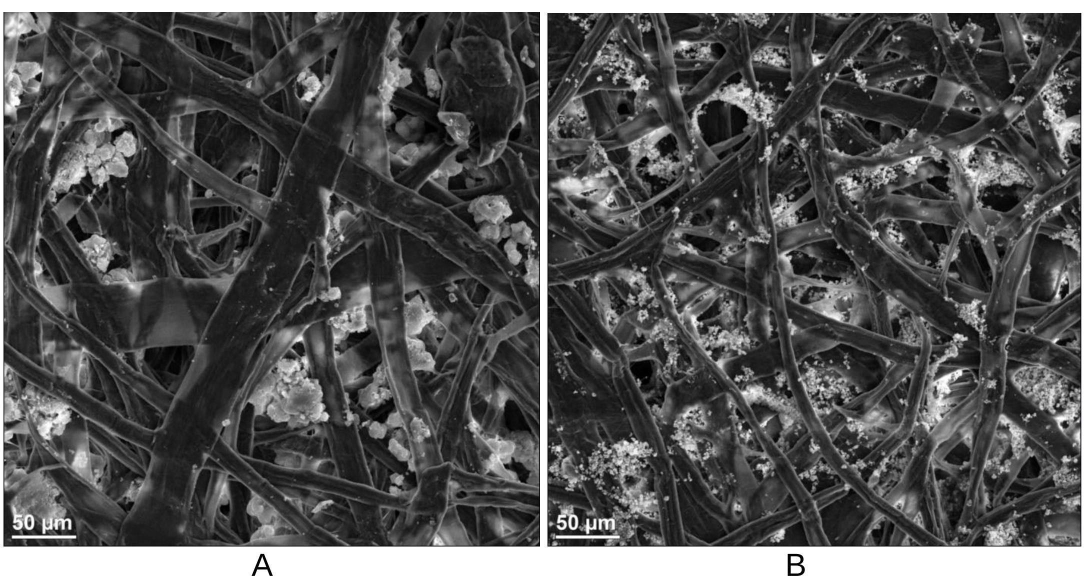

Fig. 5. Filler distribution on handsheet surfaces: A) FACS; B) PCC (20% filler content, 0.05% CPAM addition)

Effect of Filler Loading on Paper Properties

Bulk and porosity

PCC has the advantage of higher bulk when used as paper filler in comparison with ground calcium carbonate (GCC) (Won and Kim 2010). Increasing the bulk of paper can reduce the production cost of many paper grades, such as copy paper. Figure 6A shows the change of bulk with increased filler content. The bulk of the FACS-filled paper increased markedly with the FACS content, as compared to PCC filler. The bulk of the handsheets reached 2.08 cm^3/g when the FACS content was 20%, which represented an increase by around 56.4% compared to the control (without fillers, 1.33 cm^3/ g), whereas the increase for a 20% PCC-filled paper was only 9%.

The filler particle size, particle size distribution, and particle shape dominate the the bulk of paper (Velho 2002; Brown 1998). The larger particles are able to open larger inter-fiber spaces within the paper (Hubbe and Gill 2004), which contributes to the improved the bulk of paper, such is the case when FACS is used. Additionally, compared to PCC, the lower bulk density implies that more air voids exist in particles, which are partially responsible for the high bulk of FACS-filled paper (McLain and Ingle 2009).

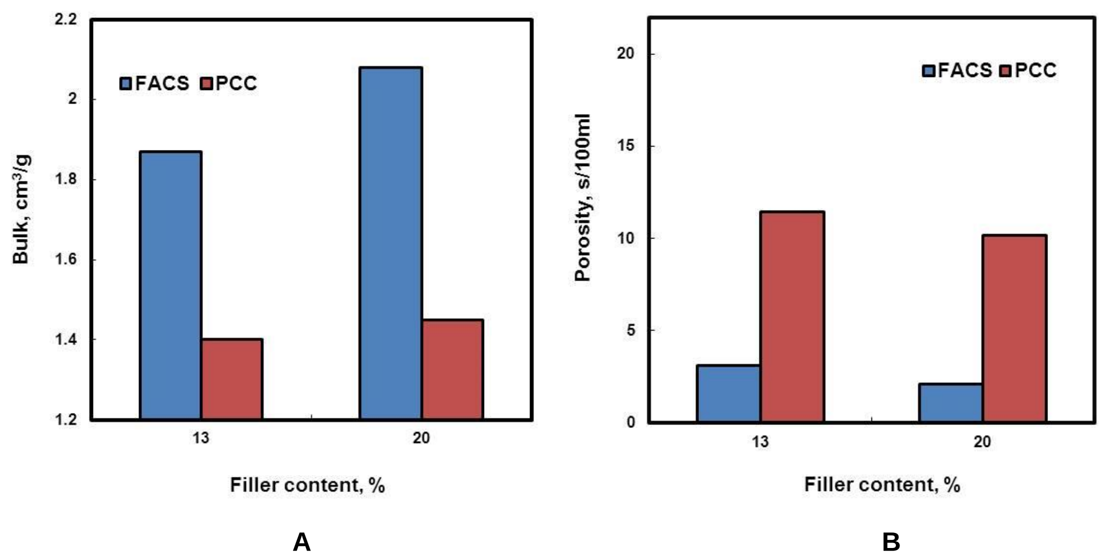

Fig. 6. Effect of filler content on the bulk of paper and porosity (0.05% CPAM)

Fillers, such as PCC and GCC, can open up sheet pores, causing an increase in paper porosity as filler loading increases. As shown in Fig. 6B, the paper porosity increased with the filler content. The porosity of FACS-filled paper was much higher than PCC-filled paper. Filler shape and particle size play an important role on the porosity (Velho 2002). The larger particle size of FACS opens up pores in paper more easily, resulting in higher porosity than PCC-filled paper. Decreasing particle size of FACS or blending with small particle size filler could be alternative ways to limit the increase in paper porosity when FACS is used as the paper filler.

Strength properties

The addition of inorganic fillers into paper will compromise the paper strength (Casey 1988 and Fatehi *et al.* 2010). As shown in Figure 7A, tensile index decreased when the filler content increased in paper. Additionally, higher tensile index could be obtained for FACS-filled paper compared to PCC-filled paper. Filler particle size and density can affect paper tensile strength by changing the number of particles for a given filler content at a similar particle size distribution. The detrimental effect of increasing filler content on tensile strength is more pronounced at a smaller particle size (Han and Seo 1997; Chauhan *et al.* 2012; Hubbe and Gill 2004). The particle size of FACS was larger than the PCC, resulting in less negative effect on fiber bonding by reducing the number of the particles. Generally, the changes in tensile and burst indices correlate (Casey 1988). As shown in Fig. 7B, the trend of the change in burst index of handsheets with different filler loading was similar to that of tensile index, as expected.

As illustrated in Fig. 7C, the bulk of paper decreased as tensile strength increased, implying that the bulk of paper can be improved by increasing filler loading at the expense of decreasing inter-fiber bonds. FACS-filled paper had a higher bulk while sustaining a higher tensile index in comparison with PCC-filled paper. This can be attributed to its special morphology, large average particle size, and low bulk density.

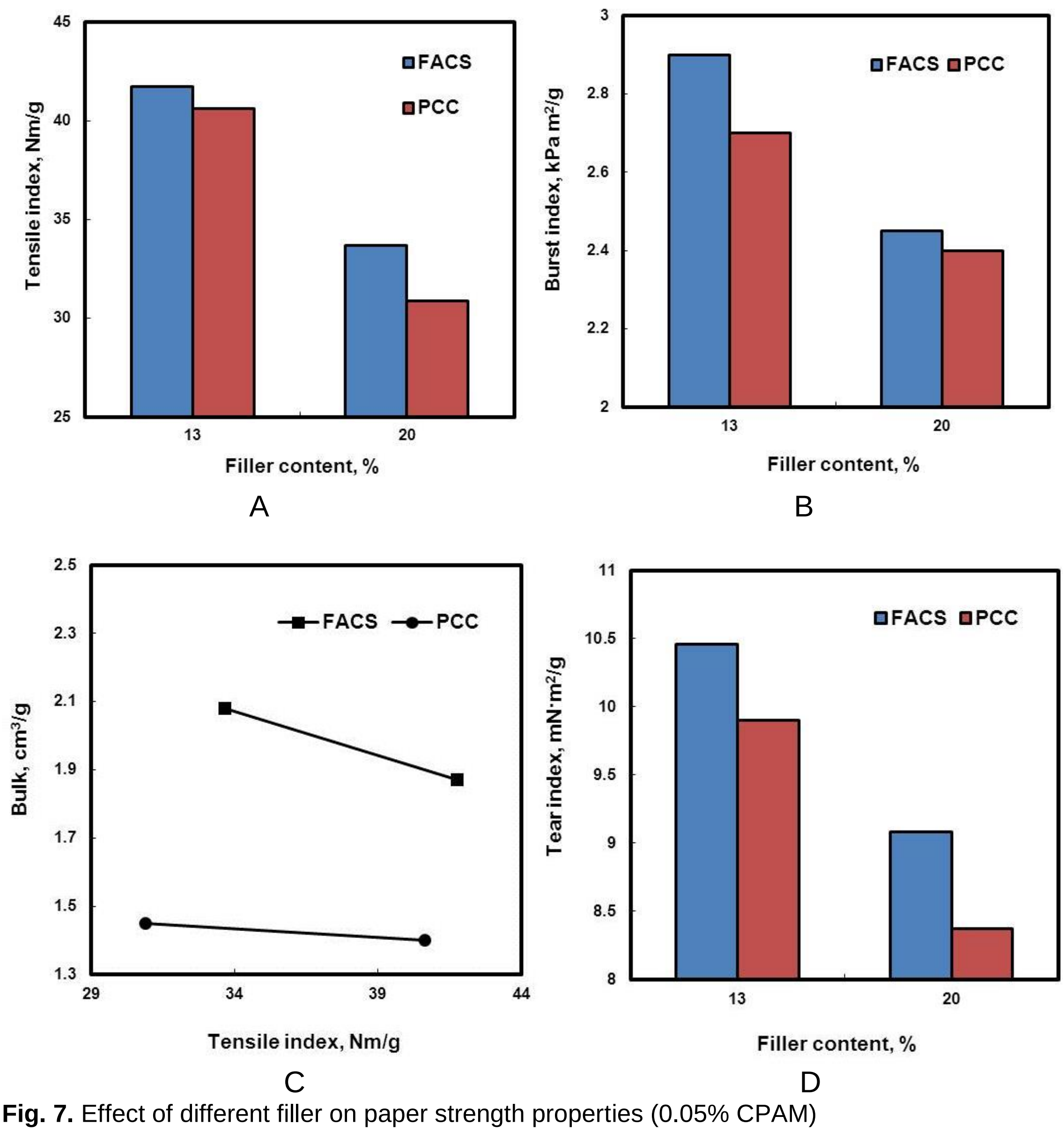

Fig. 7. Effect of different filler on paper strength properties (0.05% CPAM)

The effects of filler loading on tear strength are shown in Fig. 7D, and it can be seen that tear strength decreased as filler content was augmented. This can be explained by less fibers being available in the sheets, since tear strength mainly depends on fiber length and fiber bonding (Page and Macleod 1992; Liu *et al.* 2012; Chauhan *et al.* 2012). The tear index of FACS-filled paper was higher than that of PCC-filled paper. The porous morphology of FACS may help increase the friction between fiber and filler, which may result in higher tear strength compared to PCC.

Optical properties

The changes in brightness of handsheets with different fillers are shown in Fig. 8A. The paper brightness was increased by increasing filler loading. Due to the higher brightness of PCC filler, the brightness of PCC-filled paper was higher than that of FACS-filled paper. However, FACS filler overcame the drawback of low brightness of fly ash, as noted in earlier studies (Sinha 2008; Fan and Qian 2012), which makes it possible to be used for the production of white paper.

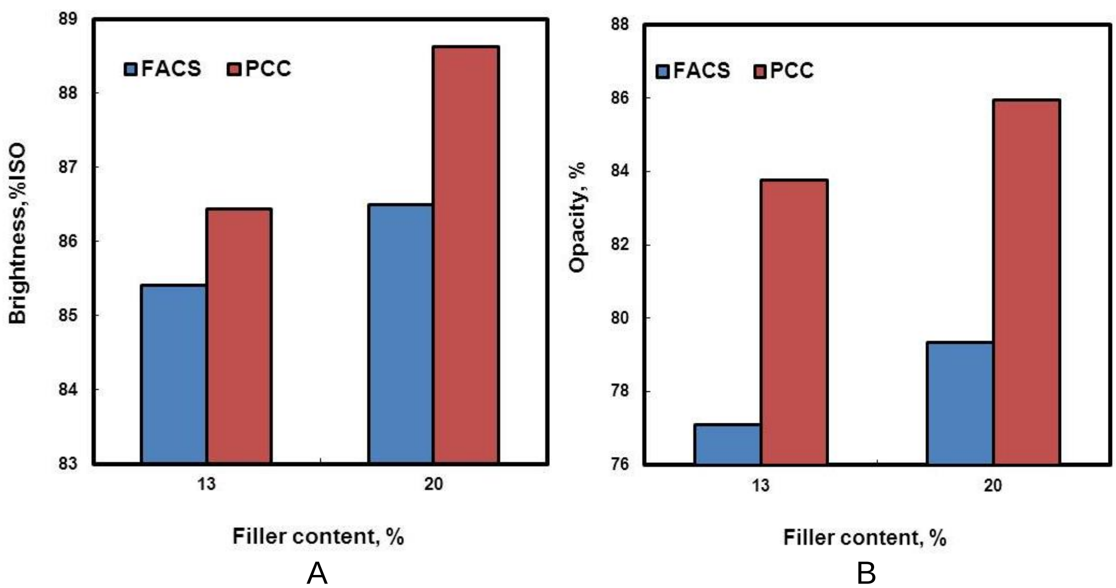

Fig. 8. Effect of filler type on optical properties (0.05% CPAM)

Figure 8B illustrates the comparison of opacity of handsheets. FACS-filled paper had good opacity; however, it was lower than PCC-filled paper. Smaller particles with narrow particle size distributions are expected to yield a higher light-scattering coefficient (McLain and Ingle 2009). FACS and PCC had similar particle size distributions but different mean particle size. The latter affected the light-scattering coefficient by changing the number of particles in the handsheets, resulting in higher opacity with the PCC-filled paper.

CONCLUSIONS

1. Fly ash-based calcium silicate (FACS) has some unique properties compared to conventional precipitated calcium carbonate (PCC) filler. The FACS filler evaluated in the present work had larger particle size, higher specific area, and lower bulk density than PCC.
2. Dynamic drainage tests indicated that FACS had similar first pass retention (FPR) and first pass filler retention (FPAR) in comparison with PCC. The addition of retention aid, such as CPAM, was able to significantly improve the FACS filler retention, although without any CPAM, the FACS retention was better than the PCC retention under the same conditions.
3. FACS was found to improve the bulk of paper remarkably, while the porosity was much higher than PCC-filled paper because of its larger and aggregated particles and lower bulk density. Additionally, the tensile, burst, and tear indices of FACS-filled paper were higher than that of the PCC-filled paper, while the brightness and opacity were lower. Based on these results, it was concluded that FACS is a potential filler to be used in the paper industry.

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