Starch/Sodium Stearate Modified Fly-Ash Based Calcium Silicate: Effect of Different Modification Routes on Paper Properties

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Different modification routes using fly ash-based calcium silicate (FACS) with starch/sodium stearate were explored to mitigate the negative effect of filler on paper strength and allow for improved filler content. The morphology of the modified fillers and the properties of the filled paper were investigated. The modification route was found to be critical to the amount of starch/sodium stearate deposited on the surface of the filler particles. The most suitable modification route using FACS filler was as follows: starch (20% dosage on o.d. filler) was cooked, filler was added, and then sodium stearate was added (4% dosage on o.d. filler). The tensile index of the FACS-filled paper could be increased by 22% at 30% filler content under the best modification route. The brightness and bulk of the filled paper were also improved. However, the opacity of the filled paper was slightly decreased due to the deposition of starch/sodium stearate on the porous surface of the filler particles.

Keywords: Starch; Sodium stearate; Modification route; Fly ash based calcium silicate; Paper properties

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INTRODUCTION

In the papermaking industry, mineral-based fillers are widely used to improve the optical properties, dimensional stability, and printability of paper products (Hubbe *et al*. 2008; Song *et al*. 2009a). Compared to biomass fibers, the prices of mineral fillers are generally lower, so substituting some cellulose fibers with mineral fillers is one of the most economical and effective ways to reduce the cost of paper products (Dong *et al*. 2008; Chauhan *et al*. 2011). Cellulose fibers are one of the most abundant, renewable, biodegradable, and biocompatible natural polymer materials. When faced with the world's resource shortage and the growing energy crisis, more and more attention is being paid to such materials. Cellulose fibers and their derivatives have been used in a variety of applications in several areas, such as the textile, paper, and packaging industries and the medical field (Li *et al*. 2015).

However, fillers weaken paper by decreasing inter-fiber bonding. To reduce the negative impact of fillers on paper's strength properties, many efforts have been made to improve strength at high filler content. These include filler blending, filler pre-flocculation, filler/fines flocculation complexing, surface filling, lumen loading, and filler modification methods (Lin *et al*. 2010; Rohaya *et al*. 2010; Laufmann and Gisella 2011; Dongil *et al*. 2012; Shen and Qian 2012; Vipul and Nishi 2013; Song 2014). Filler modification has become a very popular field of research. Starch, carboxymethyl cellulose, and cellulose esters are common organic modifiers (Shen *et al*. 2010; Cao *et al*. 2011; Huang *et al.* 2013; Gamelas *et al.* 2014; Huang *et al.* 2014, 2015). There have been some studies about starch-sodium stearate complex-modified precipitated calcium carbonate (PCC) and ground calcium carbonate (GCC). In those studies, the highlight was that the modification significantly increased filler particle size and improved the paper's physical strength (Fan *et al*. 2012, 2014).

Previous studies have demonstrated that calcium silicate material can be made from fly ash, forming a product that has been referred to as fly ash-based calcium silicate (FACS). It has a highly porous structure, has high brightness (91% ISO), and has a high specific surface area. It could therefore be used as a paper filler (Song *et al*. 2012). Although there have been some studies of the modification of GCC and PCC, the modification of FACS and the associated modification routes have not been researched before. In this work, different modification routes for filler FACS using starch/sodium stearate were studied. Different addition order caused different modifications and resulted in changes in the final paper properties, as investigated in this study.

EXPERIMENTAL

Materials

Powdered corn starch without any chemical treatment was supplied by Shaanxi Ziyuan Co., Ltd., China. Sodium stearate was provided by TianjinYongsheng Fine Chemical Co., Ltd., China. The fly ash-based calcium silicate (FACS) filler, which was provided by a coal-fired power plant, had an average particle size of 24 μm, a true density of 1.3 to 1.4 g/cm^3, a specific surface area of 121 m^2/g, and brightness of 85.6% ISO. The fiber furnish used in this study was bleached hardwood kraft pulp provided by a pulp mill in Fujian, China. This pulp was refined to 40 °SR using a PFI refiner. Cationic polyacrylamide (CPAM), used as a retention agent, was supplied by Nalco Chemical Company, Nanjing, China.

Methods

Modified FACS preparation

Modified FACS was prepared *via* three different routes, as shown below:

- Route 1: starch → cooked → added sodium stearate → added filler (FACS) suspension to the forming complex;
- Route 2: mix of starch and filler (FACS) suspension → cooked → added sodium stearate;
- Route 3: starch → cooked → added filler (FACS) suspension → added sodium stearate.

In modification route 1, the starch was cooked at 3.0% solids for 30 min at 95 °C under agitation at 400 rpm. After the starch was fully cooked, 3.0% solids sodium stearate solution was mixed with the starch at 95 °C for 30 min under agitation at 200 rpm. Then, 10% solids FACS slurry was added to the starch/sodium stearate composite. The mixture then was stirred at 95 °C for 20 min under agitation at 300 rpm.

In modification route 2, the 3.0% solids starch and 10% solids FACS slurry were heated at 95 °C for 30 min under agitation at 400 rpm. After that, sodium stearate solution was mixed into the solution at 95 °C for 20 min under mixing at 300 rpm.

In modification route 3, the process of starch cooking was the same as in route 1. After the starch was cooked, 10.0% solids FACS slurry was mixed with the starch at 95 °C for 20 min with mixing at 300 rpm. Then, 3.0% solids sodium stearate solution was added to the mixture. Then mixture was stirred at 95 °C for 30 min at 200 rpm.

The dosage of starch was 20% of the dry weight of FACS. The dosage of sodium stearate was 4% of the dry weight of FACS. The resultant modified FACS was directly used for handsheet making. It should be noted that some of the resulting slurry was removed to stand for 24 h prior to optical photograph observations.

Paper-sheet preparation and determination of paper properties

Cellulosic fiber and filler (both unmodified and modified) were sufficiently mixed and CPAM was then added. The dosage of CPAM was 0.02% on the oven-dry fiber mass. The resulting furnish was made into handsheets of grammage 65 g/m^2 using a circular laboratory sheet former. The wet sheets were pressed at 0.4 MPa for 5 min and then dried at 105±2 °C for 5 min. The handsheets were stored for 24 h at 25 °C and 50% relative humidity before physical testing. The paper properties, including the tensile index, bulk, brightness, and opacity, were tested in accordance with the relevant TAPPI test methods. The filler content was determined after the paper samples were ashed at 525 °C in accordance with TAPPI test method T211 om-93.

Scanning electron microscopy

The morphology of unmodified filler, modified fillers, unmodified-filler-filled paper, and modifier-filler-filled paper were observed using an S-4800 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Modification route was found to be critical to the filler modification. In this research the most suitable modification route for FACS filler was route 3 (*i.e.*, starch was cooked, filler was added, and then sodium stearate was added). Different results have been achieved by other researchers in studying GCC modification (Zhang 2013). In another study (Cheng 2013), it was indicated that the best starch/sodium stearate modification route for GCC was route 1 (*i.e.*, the order of addition of filler and modifier was: starch cooked; sodium stearate added; and filler added in the end).

The paper's tensile index using different modified FACS was improved to various extent (from roughly 11% to 22% relative to unmodified filler use, as shown in Fig. 1A). Fillers can decrease the paper strength because they interfere with fiber hydrogen bonding. One of the starting points of filler modification is reducing the negative impact of filling by enhancing the bonding between filler and fibers. The starch/sodium stearate complex deposited on the filler surface can bond with fibers more easily than filler particles because there are more active hydroxyls on the fiber surface.

As shown in Fig. 2, after 24 h the supernatant of R3 was the clearest, meaning that the amount of starch/sodium stearate deposited on R3 fillers was the highest. The more composite deposited on the filler particles, the better the bonding between the filler and fibers. The largest increase in the tensile index was in R3 paper, followed by R1 and R2 paper.

Figure 1B shows that the different modification routes had great effects on the bulk of the filled paper. Compared to the paper filled with unmodified filler, the bulk of the R1 and R2 papers was lower. However, the bulk of the R3 paper was slightly increased. The decrease in the bulk of the R1 and R2 papers was attributed to more starch/sodium stearate composite adsorbing to fibers instead of filler particles, thus increasing fiber bonding and decreasing bulk (He 2011). This may have been because most of the starch/sodium stearate composite was deposited on R3 filler particles, which facilitated the bonding of filler and fibers; thus, the bulk of the R3 paper was slightly increased.

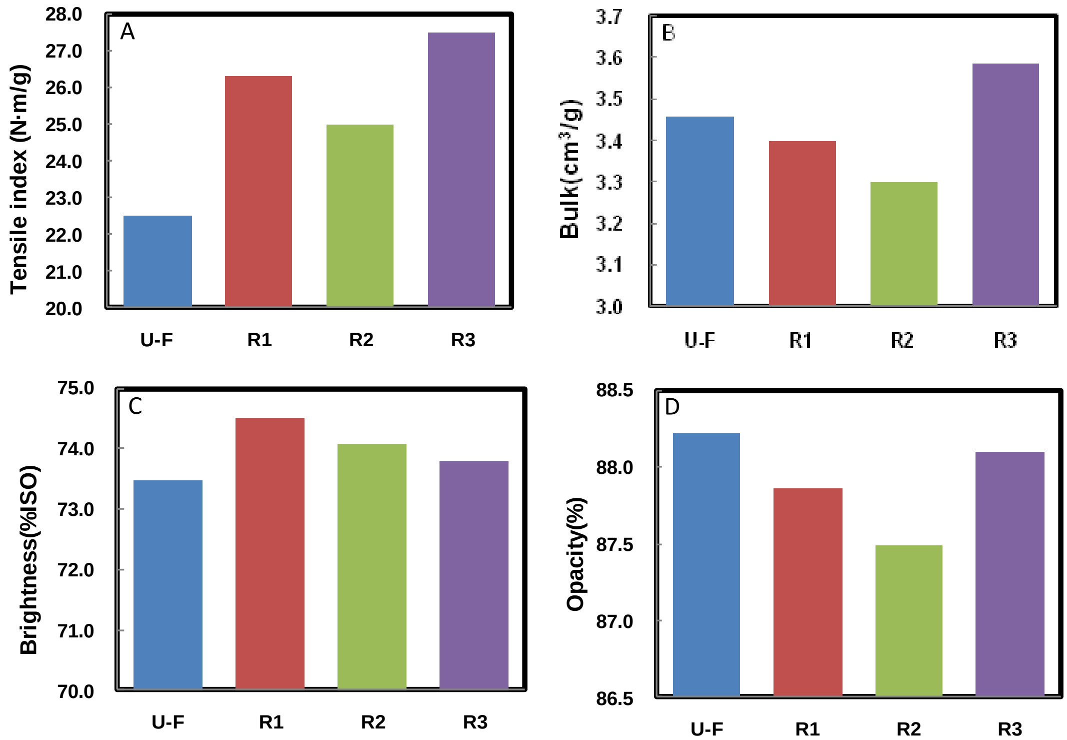


Fig. 1. Impact of different modification routes on tensile index (A), bulk (B), brightness (C), and opacity (D) of paper sheets. U-F and R1, R2, and R3 refer to unmodified FACS filler and filler prepared *via* modification routes 1, 2, and 3, respectively

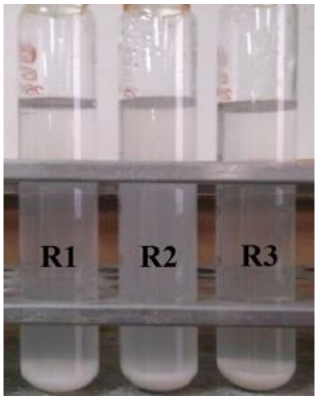


Fig. 2. Macroscopic optical photographs of different modified filler-containing aqueous mixtures. From left to right, modification routes 1 to 3. The freshly prepared aqueous mixtures were allowed to stand for 24h prior to observations

Furthermore, modified filler-filled paper had higher brightness and lower opacity, as illustrated in Figs. 1C and 1D. The starch/sodium stearate composite that was not deposited on the filler particles may have adsorbed to fibers, thus enhancing fiber-fiber bonding. Tight fiber bonding reduced the optical scattering of paper and decreased its opacity. However, significant amounts of starch/sodium stearate composite were deposited on the filler particles prepared *via* route 3, which increased the non-optical contact area of the paper. Hence, the opacity of the R3 paper was slightly decreased.

SEM images of FACS are shown in Fig. 3. They show that the surface of the unmodified filler was porous. No matter the modification route used, the porous surface of the FACS filler was negatively affected after being modified and the optical scattering ability of the FACS fillers was reduced, thus decreasing the resulting paper's opacity.

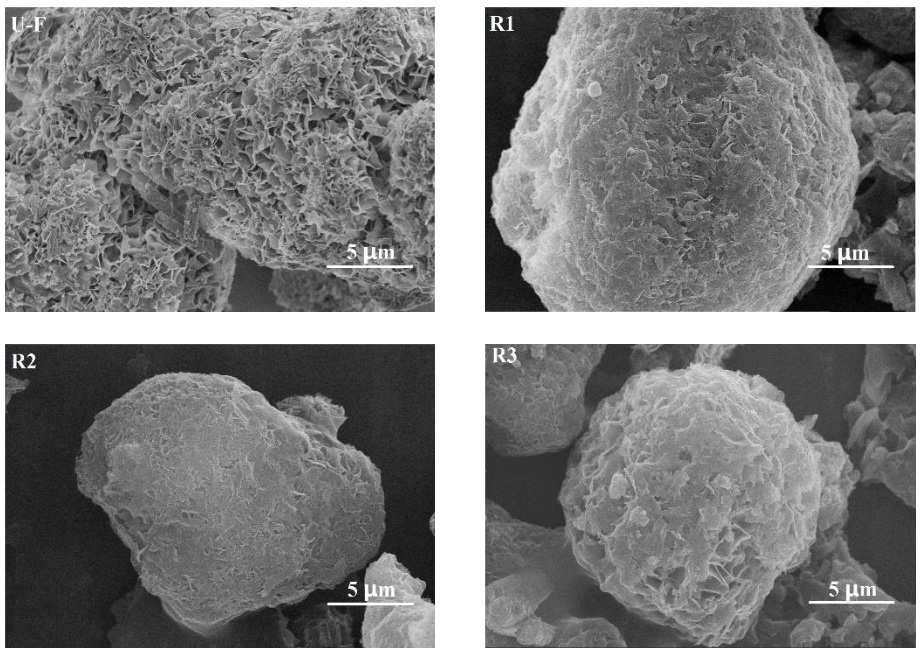


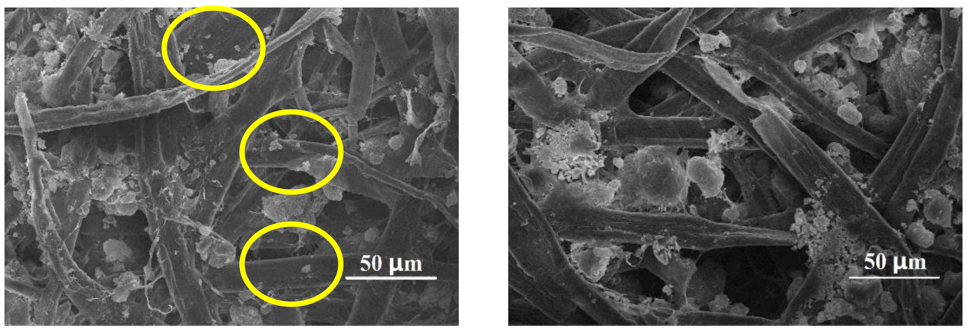
Fig. 3. SEM images of differently modified fillers. U-F: traditional filler; R1: modification route 1 filler; R2: modification route 2 filler; R3: modification route 3 filler

The brightness of paper depends on the filler brightness (Zhang *et al*. 2013). The brightness of the FACS and starch used in this research were 85.6 and 91.06% ISO, respectively. Because of the normally low brightness of the FACS, increasing the modified filler's brightness may have caused the increase in the paper's brightness. However, the composites on the filler particles had a higher optical absorption coefficient, which caused a negative effect on the paper brightness. This is why the brightness of the R3 paper was increased slightly.

In summary, modification route 3 resulted in a comprehensive improvement in the tensile index, bulk, and brightness, while the opacity of the filled paper was slightly decreased.

Starch had many free hydroxyl groups after it was cooked. These free hydroxyl groups could react with the fibers' free hydroxyl groups to form hydrogen bonds, improving the paper's tensile strength. Smaller particles have relatively larger specific surface areas, which allow them to more readily absorb chemicals. FACS was added to the cooked starch in this modification route. Some of the starch was absorbed onto the surface of the smaller particles under agitation and some of the starch was absorbed to the larger particles. When sodium stearate was added, it reacted with starch and formed the starch/sodium stearate complex. The complex helped flocculate the small particles and facilitated combinations between small and large particles.

Figure 4 shows the unmodified filler-filled paper and the R3 paper. The amount of smaller-particle filler in the paper decreased after filler modification (shown in the circle in Fig. 4a). Modification contributed to decreasing the percentage of smaller particles. Starch deposited on the filler surface also enhanced the hydrogen bonding between the fibers and filler particles. This may be why modification R3 was the most suitable for FACS filler.



(a) (b)

Fig. 4. SEM images of (a) unmodified filler-filled paper and (b) modification route 3 filler-filled paper

The different modification results for different fillers (GCC and FACS) show that the modification route is crucial. Route 3 was the most suitable for FACS perhaps because a lot of silanol groups are present on the filler surface. These silanol groups can aid in the deposition of the starch/sodium stearate composition.

CONCLUSIONS

1. The modification route is critical to the effective deposition of the starch/sodium stearate complex on the filler surface. The most suitable modification route for the FACS filler was: starch cooked; filler was added; and sodium stearate was added in the end.
2. The best modification route increased the tensile index by almost 22% at 30% filler content. Meanwhile, the brightness and bulk of the filled paper were improved and the opacity of the filled paper decreased slightly. Macroscopic optical images and SEM observations of the fillers confirmed the surface deposition effect of the modifiers on the filler.

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