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Short communication

Filler modification for papermaking with starch/oleic acid complexes with the aid of calcium ions

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ABSTRACT

To mitigate the negative effect of filler addition on paper strength and improve filler retention, filler modification with hydrogen bonding polymers (e.g., starch) or their composites is an interesting research topic. Differing from previous reports, the concept related to the deposition of starch/oleic acid complexes on precipitated calcium carbonate (PCC) with the aid of calcium ions was demonstrated. The introduction of calcium ions resulted in effective starch deposition. As a result of filler modification, filler retention and the tensile strength of the filled paper were simultaneously improved essentially due to the aggregation of PCC particles in filler modification process as well as improved filler bondability. The concept demonstrated in this brief study may provide an alternative approach to filler bondability enhancement for improved papermaking performances.

1. Introduction

In the paper industry, the use of mineral fillers such as clay and calcium carbonate in paper production is a well-established practice. The use of fillers is known to contribute to cost and energy savings (Cheng, Broadus, & Ancona, 2011; Dong, Song, Patterson, Ragauskas, & Deng, 2008). Another benefit associated with the use of mineral fillers is that many critical properties of traditional paper products, such as optical properties and printability/writability, can be improved. Furthermore, the use of specialty fillers can confer special functions such as photocatalytic properties to cellulosic paper (Shen, Song, Qian, & Ni, 2011).

However, a challenge associated with the use of fillers, especially at high addition levels, is related to poor filler retention and the detrimental effect on paper strength. Once these negative impacts are mitigated to a certain degree, there would be huge potential of further cost/energy savings by using higher amounts of fillers. In this regard, various concepts have been proposed and demonstrated. These include but not limited to filler preflocculation (Sang, McQuaid, & Englezos, 2012), complexation of fillers with cellulosic fines (Subramanian, Fordsmand, Paltakari, & Paulapuro, 2008), and surface modification of fillers (Shen, Song, Qian, & Liu, 2009).

Various polymers can form hydrogen bonds with cellulosic fibers, and thus they can be used as papermaking strength additives (Bai, Hu, & Xu, 2012; Fatehi, Kititerakun, Ni, & Xiao, 2010; Ghasemian, Ghaffari, & Ashori, 2012). Likewise, filler modification with hydrogen bonding polymers or their composites to mitigate the negative effect of filler addition on paper strength, or improve filler retention, has been demonstrated (Cao, Song, Deng, & Ragauskas, 2011; Deng, Jones, McLain, & Ragauskas, 2010; Fatehi, Hamdan, & Ni, 2013; Shen, Song, & Qian, 2009; Shen, Song, Qian, & Yang, 2010; Yan, Liu, & Deng, 2005; Yoon & Deng, 2006a, 2006b; Zhao, Hu, Ragauskas, & Deng, 2005). It has been reported that starch/fatty acid complexes can be anchored on filler particles with the aid of acids to enhance the performance of fillers (Cao et al., 2011; Deng et al., 2010; Shen, Song, & Qian, 2009; Yoon & Deng, 2006b); however, such an approach may not be easily applied to the widely used calcium carbonate fillers due to their acid-unstable nature. In view of this, differing from previous reports, the concept of precipitating starch/oleic acid complexes on filler particles with the aid of calcium ions was demonstrated in this study. It was assumed that such a concept could be readily applied to calcium carbonate fillers.

2. Experimental

2.1. Materials

Precipitated calcium carbonate (PCC) filler with brightness of 92.4% ISO was obtained from Guangxi Guilin Wuhuan Co., Ltd., China. Unmodified corn starch with dryness of 90.65% was

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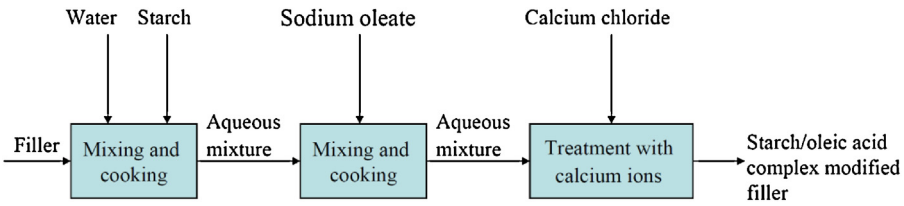

Fig. 1. Process flow of filler modification with starch/oleic acid complexes with the aid of calcium ions.

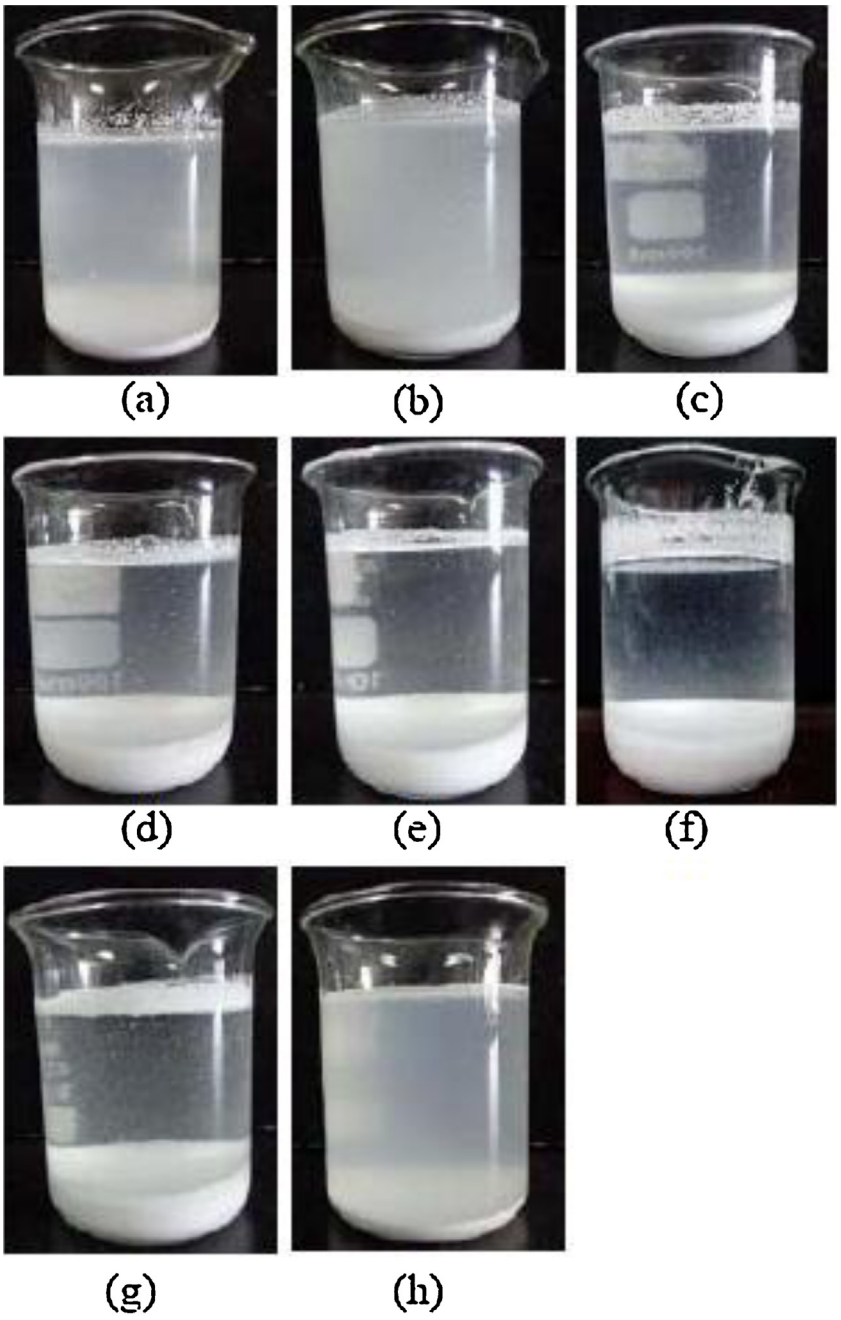

Fig. 2. Macroscopic optical photographs of modified-PCC-containing aqueous mixtures: (a)–(g) modified PCC slurries prepared at sodium oleate dosages of 0, 0.2%, 0.4%, 0.6%, 0.8%, 1.0%, and 1.2%, respectively; (h) modified PCC slurry prepared at sodium oleate dosage of 0.4% without calcium ion treatment. *Note*: (1) for (a)–(h), starch dosage was 20%, and the slurries were stored (in a stationery manner) for 24 h before photographs were taken; (2) for (a)–(g), the cooked starch/PCC/sodium oleate mixtures were poured into 0.2 mol/l calcium chloride solution to prepare modified PCCs; (3) for (h), the cooked starch/PCC/sodium oleate mixture was not treated with calcium chloride.

provided by Shandong Runyin Biochemical Engineering Co., Ltd., China. Sodium oleate of analytical grade was supplied by Tianjin Yongda Chemical Reagents Co., Ltd., China. All of the above-mentioned materials were used as received. The bleached chemical pulp used for paper-sheet preparation was provided by Mudanjiang Hengfeng Paper Co. Ltd., China, and was refined in a Valley beater to a beating degree of 31 °SR.

2.2. Filler modification

To a four-necked flask, 3 g of starch and 15 g of PCC (both on a dry-weight basis) were added. Distilled water was then added, and the total weight of the mixture was adjusted to 100 g. The mixture was then mixed by stirring at 200 rpm using a metal stirrer. Under stirring at 200 rpm, the mixture was heated to 95 °C using a water bath and cooked for 1 h at this temperature. Afterwards, 50 g of sodium oleate solution (prepared by mixing sodium oleate with distilled water) was added (sodium oleate dosages of 0, 0.2%, 0.4%, 0.6%, 0.8%, 1.0%, and 1.2% were explored in this study), and the resulting mixture was cooked at 95 °C for 30 min. After cooling down to about 30 °C, the mixture was diluted to a total volume of 500 ml; under stirring at 200 rpm 200 ml of which was poured into 200 ml of 0.2 mol/l calcium chloride solution to induce the deposition of starch/oleic acid complexes on PCC. The slurry was finally washed by centrifugation to remove the excess calcium ions. This resulting slurry was directly used for paper-sheet preparation.

2.3. Estimation of starch deposition in filler modification process

Upon the completion of filler modification, the modified filler slurries were stored (in a stationery manner) for 24 h. Photographs of the slurries were then taken for observations. Also, the supernatants were collected for turbidity analysis using a WGZ-200 turbidity tester (China) with a measuring range of 0 to 200 NTU. The turbidity can be an indication of starch deposition efficiency (Shen et al., 2010). In general, a low turbidity corresponds with a high deposition efficiency.

2.4. SEM observations of fillers

For morphology analysis, scanning electron microscopy (SEM) observations of the fillers was performed using a scanning electron microscopy (SEM, QUANTA 200).

2.5. Paper-sheet preparation and determination of paper properties

The aqueous slurry containing pulp and filler were mixed at 200 rpm for 2 min using a metal stirrer. Subsequently, paper-sheets with target basis weight of 63.7 g/m^2 were prepared using a ZQJ1-B-II sheet former (China). The wet-sheets were pressed at 0.4 MPa for 5 min, and then dried for 5 min. The target filler addition level was 20%, based on the total dry weight of pulp and filler.

The tensile strength of paper-sheets was determined using a ZL-300A strength tester (China). The brightness and opacity of paper-sheets were tested using a YQ-Z-48A brightness & color tester (China). Paper thickness was tested using a ZUS-4 paper thickness tester (China), and paper density was then calculated.

Table 1
Turbidity of the supernatants of various modified filler slurries shown in Fig.2.

Sample shown in Fig. 2	Supernatant turbidity (NTU)
Fig. 2(a)	BMR
Fig. 2(b)	BMR
Fig. 2(c)	15.3
Fig. 2(d)	11.4
Fig. 2(e)	9.1
Fig. 2(f)	8.6
Fig. 2(g)	8.5
Fig. 2(h)	BMR

Note: BMR refers to beyond the measuring range (i.e., >200 NTU).

2.6. Evaluation and estimation of filler retention

The filler-containing paper-sheets were incinerated at 525 °C, and the ash weight was calculated. Filler retention was calculated using the following equation (Shen et al., 2010):

$$R(\%) = \frac{A_1 - A_2}{A} \times 100$$

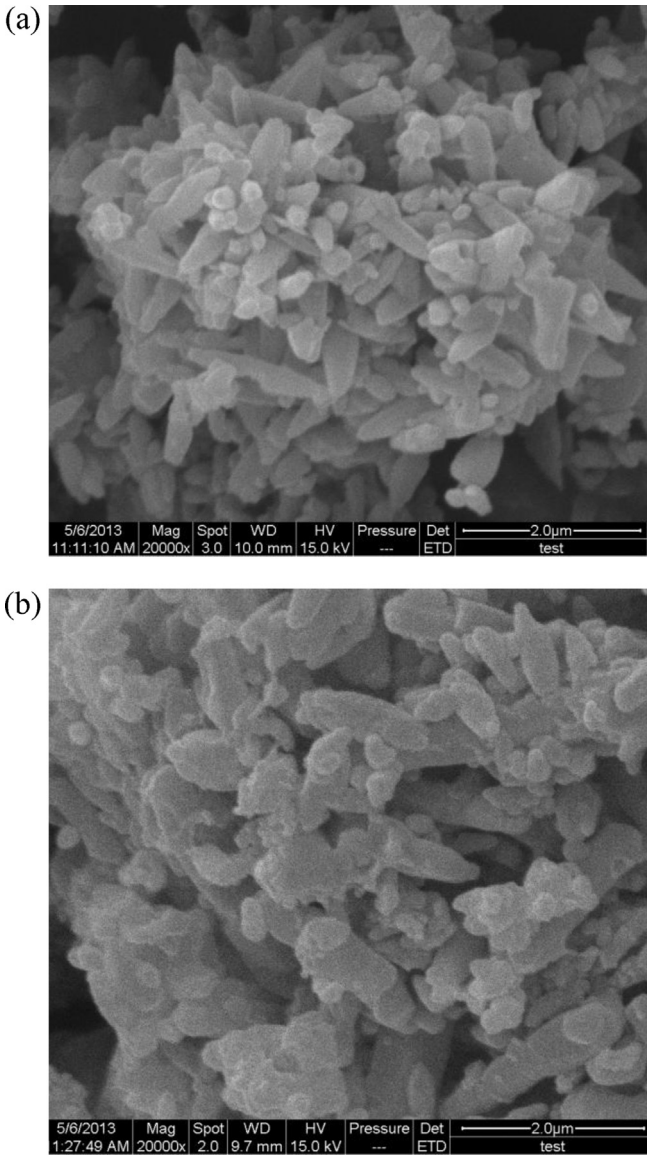

Fig. 3. SEM images of (a) PCC and (b) modified PCC (starch dosage: 20%; sodium oleate dosage: 0.4%).

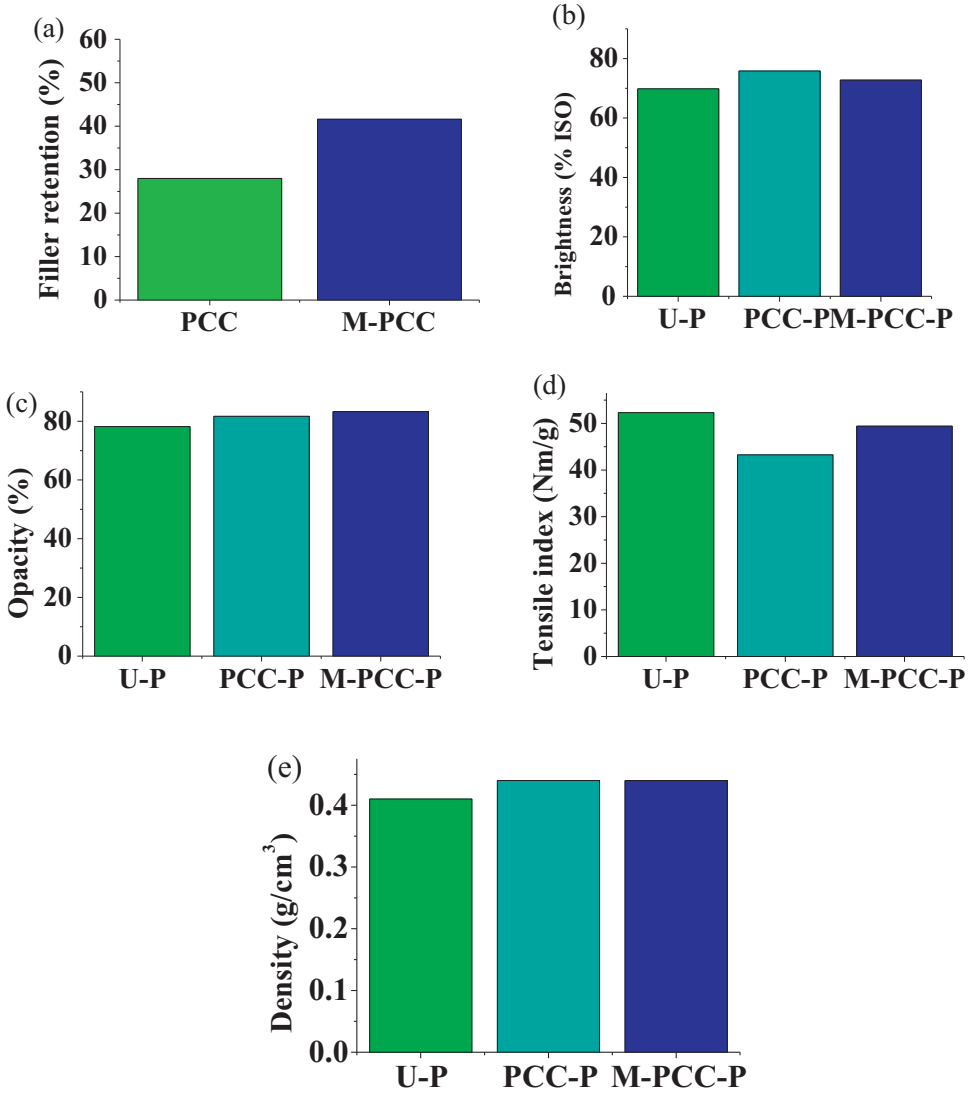

Fig. 4. Effect of filler modification on filler retention and the properties of filled paper: (a) filler retention; (b) brightness; (c) opacity; (d) tensile strength; (e) density. *Note*: M-PCC refers to modified PCC; U-P, PCC-P, and M-PCC-P refer to unfilled paper, PCC-filled paper, and modified-PCC-filled paper, respectively.

where A_1 is the total weight of ash in the sheet, A_2 is the weight of ash in the sheet originating from pulp fibers, and A is the weight of filler incorporated in each sheet.

3. Results and discussion

3.1. Proposed process concept of filler modification by deposition of starch/oleic acid complexes on filler particles with the aid of calcium ions

The encapsulation of filler particles with starch or its composites is an interesting concept to improve the strength properties of filled paper through enhanced fiber-to-fiber bonding (Cao et al., 2011; Deng et al., 2010; Shen, Song, & Qian, 2009; Yan et al., 2005; Yoon & Deng, 2006a, 2006b; Zhao et al., 2005). This concept may also lead to aggregation of particles, and hence increased filler retention. It has been reported that starch/fatty acid complexes can be precipitated on filler particles with the aid of strong/weak acids (Cao et al., 2011; Deng et al., 2010; Shen, Song, & Qian, 2009; Yoon & Deng, 2006b); however, this approach may not be suitable for modification of calcium carbonate fillers, as dissolution would occur. In this study, an approach of filler modification by deposition of starch/oleic acid complexes on filler particles with the aid of calcium ions was proposed (see Fig. 1). The aqueous starch/filler mixture is cooked to allow sufficient starch gelatinization, and thus each filler particle is surrounded by several starch molecules. The subsequent addition of a water-soluble sodium oleate to the cooked starch/filler mixture would initiate the formation of starch/fatty acid complexes (oleic acid molecules enter into the helical structure of starch) (Cao et al., 2011; Deng et al., 2010; Shen, Song, & Qian, 2009; Yoon & Deng, 2006b). Finally, the interaction of starch/oleic acid complexes with calcium ions (oleic acid can be precipitated by calcium ions) would allow their deposition on filler particles. It is evident that as no acid is introduced, this approach may readily be applied to calcium carbonate fillers.

It was found that in the presence of sufficient amount of calcium ions, the dosage of sodium oleate was critical for efficient starch deposition. As shown in Fig. 2(a)–(g), at the sodium oleate dosage of 0.4% or higher (based on the dry weight of PCC), the supernatant of modified filler slurry was quite clear, indicating efficient precipitation of starch (Shen et al., 2010). However, when calcium ions were not introduced, the supernatant was quite turbid (see Fig. 2(h)); thus, the presence of trace amount of original calcium

ions in PCC was not able to induce efficient starch precipitation. The results shown in Table 1 agree well with the observations from Fig. 2. It is clear that the use of sodium oleate and excess calcium ions plays an important role in starch deposition.

As shown from the SEM images (see Fig. 3), the surface morphology of the modified PCC was substantially different from that of unmodified PCC, indicating the efficient adsorption of starch/oleic acid complexes on PCC. It can also be seen that in addition to surface encapsulation with starch-based composites, filler modification also resulted in some kind of aggregation of PCC particles. This agrees with the published reports on filler modification with starch/fatty acid complexes in the presence of strong or weak acids (Cao et al., 2011; Deng et al., 2010; Shen, Song, & Qian, 2009; Yoon & Deng, 2006b).

3.2. Use of modified PCC in papermaking

In this study, the dosage of starch for filler modification was fixed at 20%, based on the dry weight of PCC. As discussed earlier (3.1 Proposed process concept of filler modification by deposition of starch/oleic acid complexes on filler particles with the aid of calcium ions), at the sodium oleate dosage of 0.4% or higher, filler modification resulted in efficient deposition of starch/oleic acid complexes on PCC. Thus, the modified PCC prepared at starch and sodium oleate dosages of 20% and 0.4%, respectively, was used for evaluation in terms of its performance as a filler material in papermaking. The results are shown Fig. 4. PCC modification significantly improved filler retention by 48.7% (see Fig. 4(a)), due to the aggregation of filler particles during the starch precipitation process (see Fig. 4). Another noticeable finding is that the tensile strength of modified-PCC-filled paper was 14.2% higher than that of PCC-filled paper (Fig. 4(d)). Thus, it can be concluded that filler modification substantially improved the bondability of PCC, resulting in mitigated negative effect of filler addition on paper strength. Filler modification also improved paper opacity (Fig. 4(c)), due to the increased PCC content in the sheet. The slight decrease in paper brightness (Fig. 4(b)) might be explained by the brownness of oleic acid. Additionally, filler modification was not found to have a significant effect on paper density (Fig. 4(e)).

4. Conclusions

Differing from previous reports, the concept of filler modification by deposition of starch/fatty acid complexes with the aid of calcium ions to improve its use in papermaking was demonstrated. The introduction of calcium ions induced the effective deposition of starch/oleic complexes on PCC. Filler retention was increased due to the aggregation of PCC particles in filler modification process, and the tensile strength of paper was simultaneously improved due to enhanced filler bondability. These findings may provide an alternative approach to increasing the filler content of cellulosic paper while maintaining its critical properties.

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