STARCH-SODIUM STEARATE COMPLEX MODIFIED PCC FILLER AND ITS APPLICATION IN PAPERMAKING

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The use of fillers tends to reduce paper strength, which can limit their application. Therefore research on filler modification is of significant importance in order to overcome this limitation. In this paper, precipitated calcium carbonate (PCC) was modified by starch, sodium stearate, and the starch cross-linking agent sodium hexametaphosphate. The purpose of this research is to provide useful references to the industrial application of modified precipitated calcium carbonate (PCC). Modified precipitated calcium carbonate (PCC) was characterized by particle size analyzer and scanning electron microscope (SEM). The analysis showed that the particle size of the modified PCC was significantly increased versus the control. The morphology of modified PCC also greatly changed. The influence of modified and unmodified PCC filled paper on paper physical performance was studied. The experimental results showed that at the same ash content, modified PCC filled paper compared with unmodified PCC filled paper had higher brightness, lower opacity, and higher physical strength. The impact of modified and unmodified PCC on stock retention and the comparison between modified and unmodified PCC were investigated. The experimental results showed that the stock filled with modified PCC had better retention compared to those filled with unmodified PCC.

Keywords: Starch; Sodium stearate; PCC; Sodium hexametaphosphate; Paper performance

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INTRODUCTION

High ash content paper has become an important trend in papermaking technology in recent years. The use of mineral fillers is considered to have the following advantages (Yuan 2008; Shen *et al.* 2007; Lu *et al.* 2010): substituting mineral fillers for more expensive fibers in paper stock can reduce operating and raw materials costs; fillers can improve paper optical properties; and fillers can improve sheet formation, paper dimensional stability, printability, and appearance. However, as the filler loading is increased, especially at high loading levels, filler has many limitations (Han 2009; Shen *et al.* 2009; Bai and Fan 2011): paper strength is inevitably reduced by mineral fillers because fillers can affect the fiber-fiber bonding; increasing filler levels can lower its retention, resulting in higher solid content of the white water circulation and requiring improved retention strategies; and strength-enhancing chemical additives may be needed to make up for the loss in strength.

Although traditional filler technology has a lot of advantages, it still faces many difficulties. To overcome or alleviate the disadvantages, filler modification technology has become a hot topic. Many approaches have been used or studied previously to increase the proportion of filler without sacrificing paper properties such as: preflocculation of the filler, modification of filler, lumen loading, synthesized filler, and incorporation of polymers in the sheet. Zhao *et al*. (2005) modified PCC with starch using operations including mixing, dewatering, grinding, and aggregate-break-up. It has been shown that paper filled with modified PCC had better properties such as tensile, tear, and folding strengths. Yoon and Deng (2006a) modified clay with starch precipitated with ammonium sulfate. A clay-starch mixture was cooked and put into ammonium sulfate solution. After stirring the solution, starch was precipitated on the surface of clay. It has been shown that this clay modification can markedly improve paper strength properties. Kurrle (1996) patented the modification of calcium carbonate fillers with starch-soap complex. It has been found that this method of modification can improve sizing efficiency and strength properties of the filled papers. Yoon and Deng (2006b) modified clay with raw starch, palmitic acid, potassium hydroxide, and hydrogen chloride. It has been shown that this method of modification significantly improved strength properties of the filled papers. Shen *et al*. (2008) modified PCC filler using a complex formation method with raw starch, sodium oleate, and aluminum sulfate.

As is well known, starch has good bonding ability with wood fibers due to its three hydroxyl groups on each glucose monomer unit (Deng *et al.* 2008). Starch can be dissolved and either adsorbed or precipitated by appropriate methods. During the adsorption or precipitation, this bonding material can be located on the surface of filler, by which the paper strength will be improved by the hydrogen bonding between fibers and fillers (Yoon 2007; Zhao 2008; Yan 2005).

In this study, PCC was modified with starch, sodium stearate, and the starch cross-linking agent, sodium hexametaphosphate. Starch and sodium stearate can form a complex having low solubility in water that can be easily coated on the surface of PCC. The sodium hexametaphosphate can reduce the solubility of starch, making the complex stronger. The modification generates a strong starch layer on the PCC. The morphology and size distributions of PCC fillers and modified PCC were characterized. Their effects on paper properties and stock retention efficiency were investigated.

EXPERIMENTAL

Materials

The bleached hardwood and bleached bamboo pulp blend with a drainage degree of 38°SR and PCC fillers with a specific surface area of 1.6m^2/g were provided by Guangzhou Pearl River Special Paper Co., LTD. Corn starch was a commercial food grade material provided by Guangzhou KangYe Food Factory. Sodium stearate was provided by China Yuanhang Reagent Factory. Sodium hexametaphosphate was provided by Tianjin Yongda chemical reagents development center. Cationic poly-acrylamide retention aid was obtained from China Yuanhang Reagent Factory with a molecular weight of 7,000,000.

Preparation of Starch-Sodium Stearate Complex Modified PCC

The starch was heated at 3.0% solids for 30 minutes at 95 ^{o}C. After completion, sodium stearate was mixed into the starch at 90 ^{o}C for 10 minutes. Then the starch-sodium stearate complex and sodium hexametaphosphate cross linker was added into 20% solids PCC slurry. The mixture then was stirred at 40 ^{o}C for 20 minutes at 500 rpm. The dosage of sodium stearate was 4% of the PCC dry weight. The dosage of sodium hexametaphosphate cross linker was 1% of the PCC dry weight. The resultant modified PCC was directly used for handsheet making.

Characterization of Starch-Sodium Stearate Complex Modified PCC

The morphology of the modified filler was observed by scanning electron microscope (SEM). The measurement of modified filler size was performed by a Malvern Mastersizer 2000.

Handsheets Preparation and Determination of Paper Properties

The pulp was diluted to 0.3%, and various amounts of modified filler were added during handsheet making. After the addition of filler, diluted cationic poly-acrylamide (CPAM) was added at 0.05 wt% based on solid fiber for filler retention under stirring for 5 minutes. The handsheets were formed using a Rapid-Köthen Sheet former at a basis weight of approximately 60 g/m^2.

Tensile, bust and tear strength were measured according to the standard ISO method by L&W CE062 tensile testing apparatus, L&W burst testing apparatus, and YQ-Z-20 tear testing apparatus, respectively. Paper brightness and opacity were measured using a Testing Machine Inc. (TMI) MTCRO-TB-IC instrument. The filler content was determined by ashing the paper in a muffler oven according to the ISO method.

Retention Experiment

The establishment of regression equation

First, 10 g of oven-dry pulp was added into 1800 mL water, the pulp was disinter-grated for 30,000 rpm, then unmodified PCC or modified PCC was added, mixed uniformly, and then diluted to 2000 mL. The solution was put into a dynamic drainage jar (DDJ) whose rotation speed was 1400 rpm. Then the filtrate was collected. Secondly, the mass fraction of filtrate was determined. Thirdly, different concentrations of filtrate were prepared and their whitewater turbidity was measured with a turbidity meter. Then the turbidity-concentration working curve was made. Figure 1 shows the working curve.

Dynamic drainage test

Unmodified or modified PCC and 500 mL of mixed pulp (0.2 to 0.5 wt %) were poured into the DDJ (dynamic drainage jar), then the required polymer was added at a certain propeller speed. After mixing for a specified time, 100 mL of filtrate was collected through a 200-mesh screen, and the concentration of filtrate was calculated from its turbidity based on the previous calibration (Fig. 1), involving the filtrate concentration and filtrate turbidity.

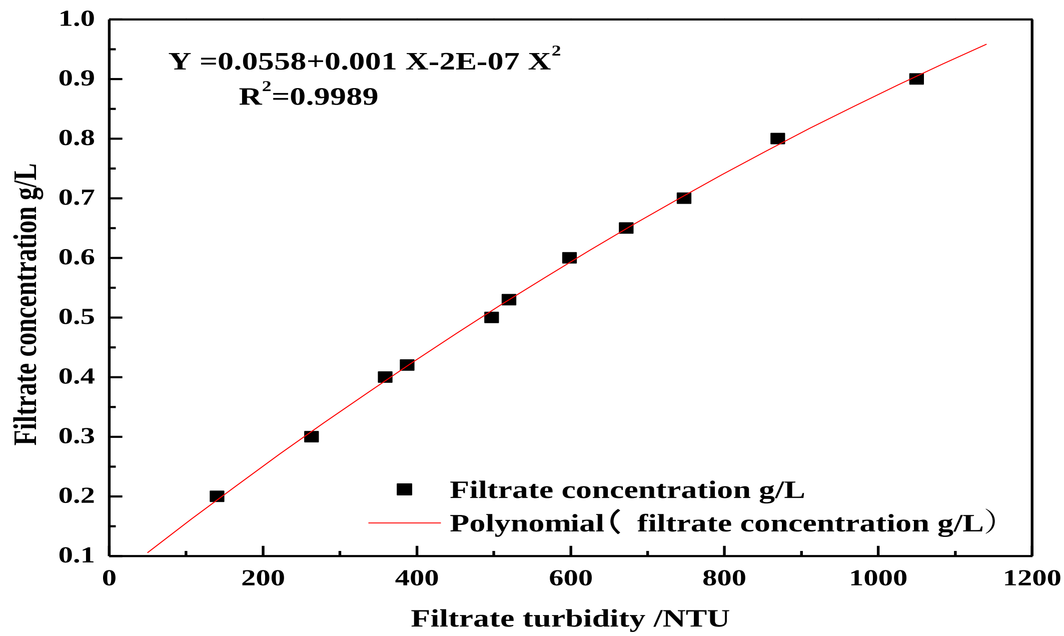


Fig. 1. Relationship between turbidity and concentration of pulp in white water

The FPR (first pass retention) was calculated by the following formula, where c_0 is the concentration of the pulp added to the DDJ, and c is the filtrate concentration.

$$FPR= (1-c/c_0) \times 100\% \quad (1)$$

RESULTS AND DISCUSSION

Characterization of Modified PCC

In order to understand the morphology of modified PCC, products were observed by SEM. The SEM pictures of unmodified PCC and modified PCC are shown in Fig. 2.

It was found that modified PCC exhibited changes with respect to morphology and particle size when compared to unmodified PCC. The edge of the unmodified PCC was sharp with small crystals visible on the PCC surface. For the modified PCC, the edge of the PCC surface was smooth, and any crystals on the PCC surface were too small to be discernible.

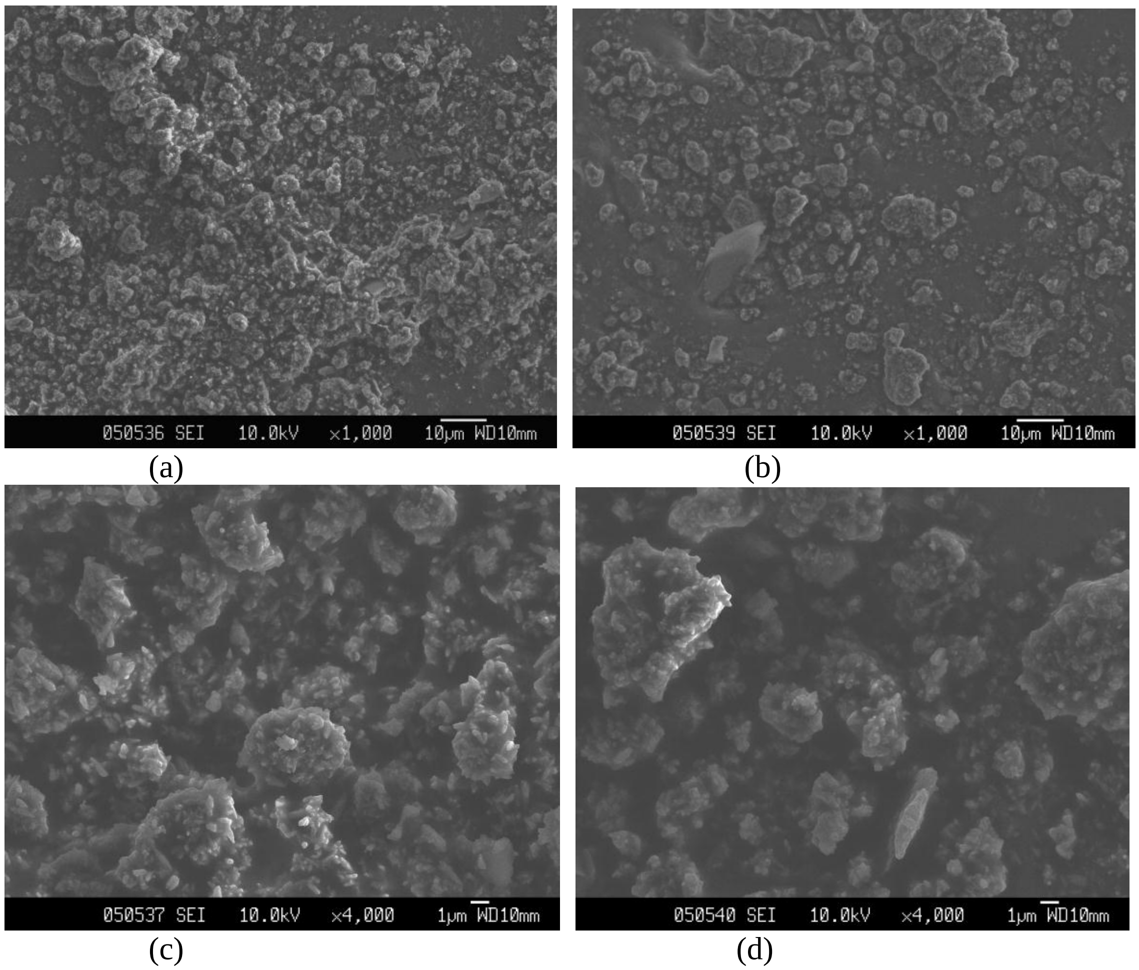
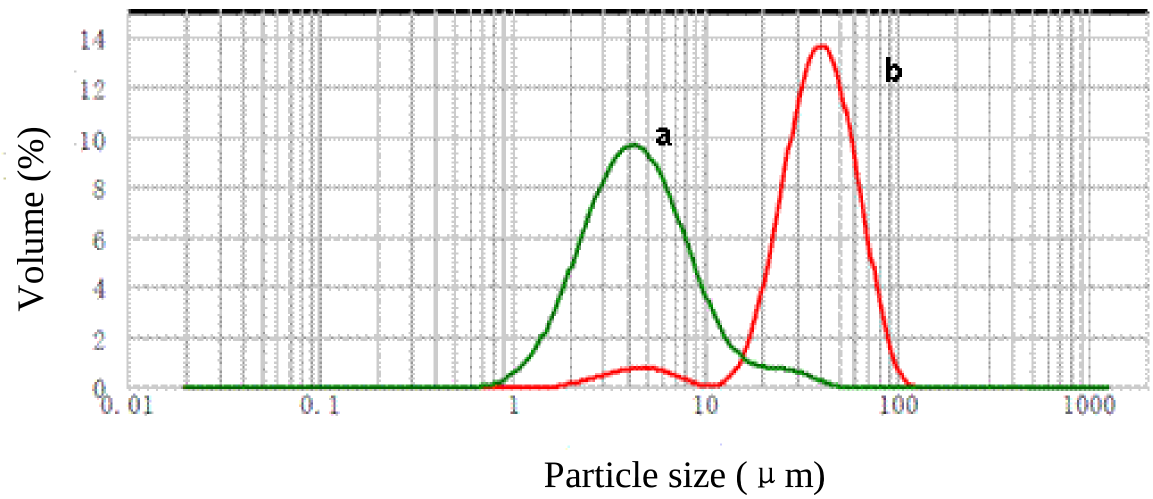


Fig. 2. SEM image of unmodified PCC and modified PCC: (a) and (b) SEM photograph of unmodified and modified PCC (×1000), respectively; (c) and (d) SEM photograph of unmodified and modified PCC (×4000), respectively

The particle size distributions of original PCC and modified PCC are shown in Fig. 3. It was found that the particle size of modified PCC was much larger than the original PCC. Modified PCC did not affect its application as a papermaking filler. The surface state of paper filled with modified PCC was very good. The larger particles can reduce the contact area between the PCC and fiber, which improves the paper strength and filler retention.



a—unmodified PCC b—modified PCC

Fig. 3. Particle size distribution of modified and unmodified PCC

Effect of Sodium Hexametaphosphate on Properties of Paper

The properties of handsheets made with different dosages of sodium hexametaphosphate modified PCC are shown in Table 1. The filler loading was 15% of the fiber dry weight. The dosage of starch was 20% of the PCC dry weight. The experimental data indicated that paper filled with modified PCC to which sodium hexametaphosphate had been added had higher brightness and lower opacity, while the physical strength of paper was greatly improved in comparison to modified PCC to which sodium hexametaphosphate was not added.

Table 1. Effect of Sodium Hexametaphosphate on Properties of Paper

Dosage of Sodium Hexametaphosphate (%)	Brightness (%)	Opacity (%)	Tensile Index (N·m/g)	Burst Index (KPa·m^2/g)	Tear Index (mN·m^2/g)
0	87.97	86.35	19.89	1.04	5.75
1	89.05	85..72	23.12	1.21	6.62

Effect of Modified PCC on Optical Properties of Paper

The brightness and opacity of handsheets made with original PCC and different dosages of starch modified PCC are shown in Figs. 4 and 5. Clearly, the increase of filler content in sheets can improve paper brightness and opacity. At the same filler content, the paper filled with modified PCC had higher brightness. At the same filler content, the paper filled with modified PCC had lower opacity compared with paper filled with unmodified PCC. However, the reduction of opacity was small.

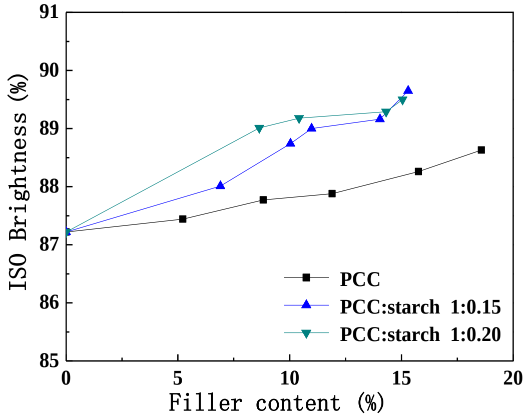


Fig. 4. ISO brightness of handsheets as a function of pure PCC and the modified PCC with different PCC to starch

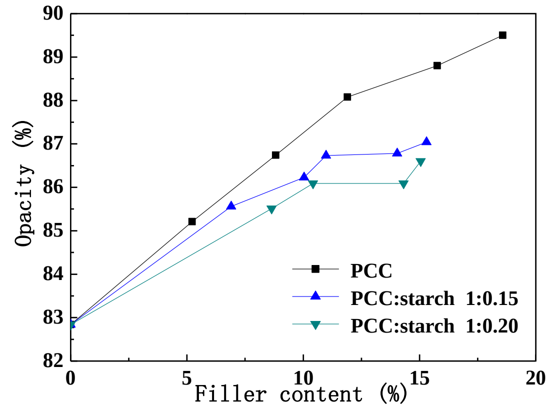


Fig. 5. Opacity of handsheets as a function of pure PCC and the modified PCC with different PCC to starch

Effect of Modified PCC on Physical Properties of Paper

Figures 6 through 8 show the effects of the modified PCC on paper physical properties. These data indicate that modified PCC could significantly improve paper strength properties when compared with original PCC. As the content of original PCC increased, the tensile, burst, and tear indices of the handsheets with original PCC decreased significantly, as shown in Figs. 6 to 8. However, the tensile, burst, and tear indices of the handsheets with PCC modified by two different starch dosages increased significantly.

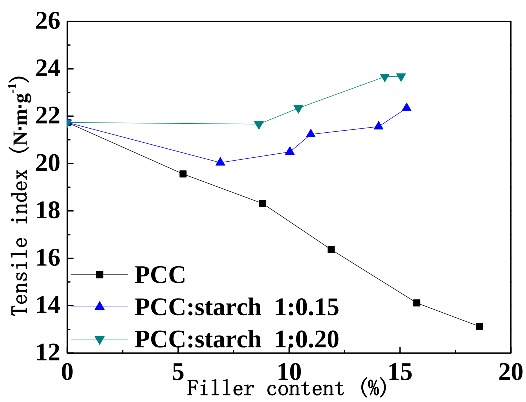


Fig. 6. Tensile index of handsheets as a function of pure PCC and the modified PCC with different PCC to starch

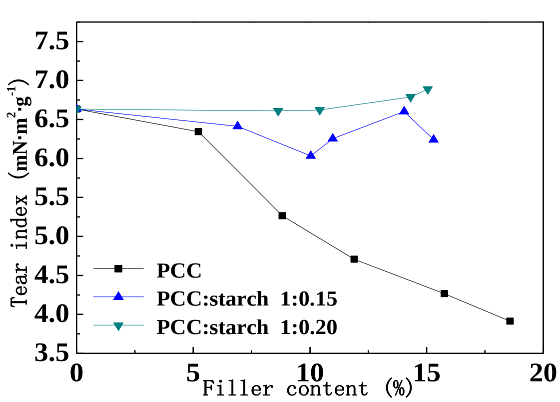


Fig. 7. Burst index of handsheets as a function of pure PCC and the modified PCC with different PCC to starch

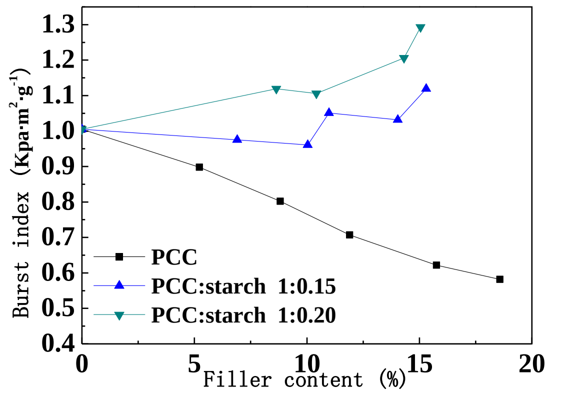


Fig. 8. Tear index of handsheets as a function of pure PCC and the modified PCC with different PCC to starch

At the same filler content, the strength of the paper filled with modified PCC was much higher than those filled with unmodified PCC. This is because at the same fiber condition, the paper strength is mainly driven by the bonding force between the fibers. The surfaces of original PCC do not have the functional groups that bond with fibers, which can interfere with the fiber-fiber bonding during handsheet formation, thereby resulting in reduced paper strength. However, the surface of modified PCC has a layer of starch, which has a good hydrogen bonding ability with wood fibers due to starch's hydroxyl groups, allowing bonding between the modified PCC and fibers. This could increase paper strength.

Effect of Modified PCC on FPR of Pulp

Unmodified and modified PCC were evaluated as papermaking filler. Handsheets with 20% filler content were produced utilizing retention aid dosages of CPAM of 0%-0.10%, a mixing time of 40s, and a mixing speed of 1500 rpm. Figure 9 shows the effect of the dosage of CPAM on the stock retention.

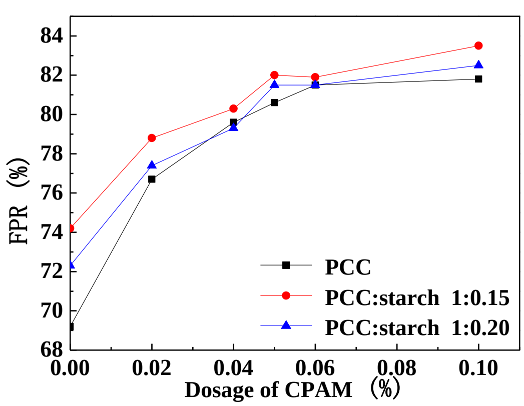


Fig. 9. Effect of the dosage of CPAM on stock retention

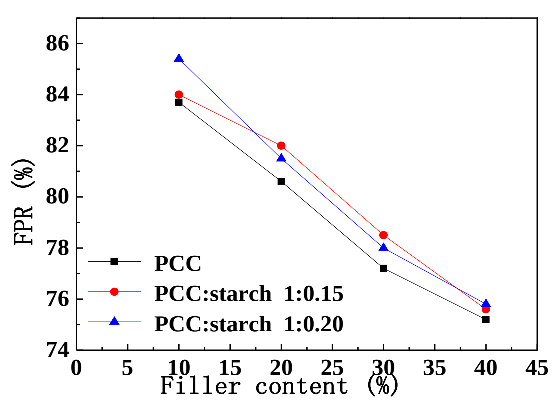


Fig. 10. Effect of the dosage of PCC on stock retention

As the dosage of CPAM increased, the retention of the stock filled with unmodified and modified PCC increased. At the same dosage of CPAM, the stock filled with modified PCC had higher stock retention when compared to unmodified PCC. This was because particle size of modified PCC is larger than unmodified PCC. The modified PCC was able to form larger floccs with CPAM and had a stronger mechanical intercepting effect during handsheet formation.

Handsheets with 10% to 40% filler content were produced utilizing a retention aid dosage of CPAM of 0.05%, a mixing time of 40 s, and a mixing speed of 1500 rpm. Unmodified and modified PCC papermaking filler were evaluated at these loading levels. As the filler content increased, the retention of stock filled with original and modified PCC decreased, as shown in Fig. 10. At the same filler content, the stock filled with modified PCC had higher stock retention in comparison to the unmodified PCC.

CONCLUSIONS

1. Modified PCC was characterized by particle size analyzer and scanning electron microscopy (SEM). The analysis showed that modified PCC particle size obviously increased when compared with unmodified PCC. The SEM analysis showed that the size and morphology of modified PCC changed greatly. These observations proved that starch addition modified the surface of PCC successfully.
2. The influence of various amounts of modified and unmodified PCC filler on paper physical performance was studied. The experimental results showed that at the same ash content, the paper filled with modified PCC compared to unmodified PCC had higher brightness and lower opacity, while the physical strength of paper was greatly improved.
3. The impact of modified and unmodified PCC on stock retention was investigated. The experimental results show that the stock filled with modified PCC had better retention compared to unmodified PCC. The retention of the stock filled with modified PCC had a better result when the dosage of starch is lower.

ACKNOWLEDGMENTS

This work was supported by the Science and Technology Plan Projects of Guangdong Province (No. 2011B010300015).

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Article submitted: March 23, 2012; Peer review completed: May 28, 2012; Revised version received: June 6, 2012; Accepted: June 8, 2012; Published: June 12, 2012.