Study of Coating Weight and Utilization Rate in the Modification of Ground Calcium Carbonate

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Ground calcium carbonate (GCC) was modified in this work using starch, sodium stearate, and sodium hexametaphosphate. The effects of reaction temperature and the dosage of sodium hexametaphosphate on the coating weight of modified GCC and the utilization rate were considered. The strength (tensile, burst, and tear) of papers filled with modified GCC *vs.* unmodified GCC was compared. The research showed that lower precipitation reaction temperature was conducive to the increase of modified GCC coating weight and the complex utilization rate. A proper dosage of sodium hexametaphosphate could effectively increase the coating weight of modified GCC and the complex utilization rate. Compared with unmodified GCC filled papers, modified GCC filled papers performed better with respect to paper strength, but the optical properties (brightness and opacity) showed the opposite trend.

Keywords: Modified GCC; Coating weight; Complex utilization rate; Precipitation reaction temperature; Sodium hexametaphosphate

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INTRODUCTION

In the modern papermaking industry, filler has become the second most prominent raw material in the product. The amount of filler can be up to 40% of the pulp stock (Beazley 1993; Griggs 1988; Wu and Zhang 2010; Lu *et al*. 2010). Many kinds of filler, such as calcium carbonate, kaolin, and titanium dioxide, have been applied in the paper industry. As alkaline filler, calcium carbonate is widely used on account of its high brightness, relatively low cost, and aptitude for the alkaline papermaking technology (Zhu *et al*. 2007; Feng *et al.* 2010; Wang *et al*. 2010). The paper's brightness, opacity, smoothness, dimensional stability, and printability can be improved by adding filler. In addition, since the cost of the filler is much lower than fiber, substituting fillers for more expensive fibers in paper stock can reduce production cost (Fan *et al*. 2012). However, fillers and fibers cannot form strong bonding because of their big differences in elements and properties. What's worse, the strength properties of papers, such as tensile, burst, and tear, are inevitably reduced as a consequence of the filler's obstruction to fibers' bonding (Zhao *et al*. 2005; Huang *et al*. 2013). To reduce the impact of fillers on the strength properties of paper, many methods have been examined, such as Lumen loading, surface modification of filler, and composite fillers (Shen *et al*. 2009; Song *et al*. 2009; Sang *et al*. 2012). Currently, surface modification of filler by organics, such as polyacrylic acid, polyvinyl acetate, carboxymethyl cellulose, and starch, has attracted considerable interest. Compared with other technologies, surface modification of filler is an effective way to mitigate the impact of filler on fiber-fiber boding ability (Mabee and Harvey 2000; Yong and Deng 2006; Shen *et al.* 2009). As is well known, starch has good bonding ability with fibers due to its hydroxyl groups on glucose monomer units. Furthermore, compared with other organic modifiers, it has many advantages, such as having good coating performance in the pasting state, as well as being widely sourced, low in cost, and environmentally friendly (Ono and Deng 1997; Mabee 2001; Yan *et al*. 2005).

In recent years, there have been a lot of studies about filler modification based on starch. Bai and Fan (2011) modified calcium carbonate with starch and showed that modified fillers can effectively improve paper strength properties. Zhang *et al*. (2010) modified GCC with corn starch, alkyl ketene dimer (AKD) and GCC, and researched the impact of the dosage of AKD on the optical properties and strength properties of modified fillers. The research showed that when the mass fraction of AKD was 15%, the overall performance of the composite filler was the best. The dosage of the modifier, concentration, reaction concentration, stirring speed, and reaction time during the filler modification, all would affect the properties of the modified filler. However, there only few studies concerned the effects of these factors on modification of filler, which is the particular focus of the present research. Barhoum *et al*. (2014) studied the effect of cationic and anionic surfactants on application of calcium carbonate in paper coating, the research just slightly concerned the coating weight of modified fillers. El-Sherbiny *et al*. (2015) and Morsy *et al*. (2014) also studied the modification of calcium carbonate, the research were not particular focus on the aspect of coating weight of modified fillers.

The effect of precipitation reaction temperature and the dosage of sodium hexametaphosphate on the coating weight of Modified GCC and the complex utilization rate were considered in this paper. At the same time, the used effects of modified GCC and unmodified GCC filled paper were investigated.

EXPERIMENTAL

Materials

Ground calcium carbonate (GCC) was supplied from Henan Tianbang Co., Ltd., China. Corn starch was provided by Shenzhen Taigang Food Co., Ltd., China. Sodium stearate was obtained by Tianjin Kermel Chemical Reagent Co., Ltd., China. Sodium hexametaphosphate was provided by Tianjin Yongda Chemical Reagent Development Center (China). The bleached eucalyptus pulp with a drainage degree of 32 °SR was supplied by Henan Tianbang Co., Ltd., China.

Methods

Preparation of starch- sodium stearate complex modified GCC

A 15% corn starch and GCC suspension (starch:GCC weight ratio = 1:5) was dispersed in cool water for 10 min under stirring at 200 rpm and then heated to 95 °C for 50 min. After this, 4.0% (based on the dry weight of GCC) sodium stearate complex solution was added to starch and GCC suspension for 30 min. Then, the temperature was dropped to certain levels (40 °C to 90 °C). After 30 min, 0% to 3% (based on the dry weight of GCC) of sodium hexametaphosphate solution was poured into the mixture solution for 30 min in the presence of stirring at 200 rpm. Finally, the modified GCC was obtained (40 °C to 90 °C) and directly used in papermaking.

Handsheet preparation

The solid contents of pulp stock and modified GCC were measured, respectively, after being dried in the oven. Then the 3g bone dry pulp stock and modified GCC with 100ml water were defibrated with the speed at 3000 rpm for 100 seconds in the disintegrator. After this, cationic poly-acrylamide (CPAM) was added at 0.05% based on fiber solids for filler retention. Finally, the modified GCC was directly used for handsheet making, and the filler loading was varied from 30% to 55%. The handsheets were formed using a manual sheet former at a basis weight of approximately 72 g/m^2.

The calculation of the coating weight of modified GCC and the complex utilization rate

At a certain constant-weight, modified GCC and GCC were incinerated at 575 °C for 4 h or more until successive tests yielded constant weight and the ash weight, based on the calculations. The starch coating weight can be expressed as the percentage of starch/sodium stearate complex in modified GCC and calculated with Eq. 1.

$$C(\%)=\frac{(1-\alpha)m_1-m_2}{m_2}\times 100 \tag{1}$$

where C is the coating weight of modified GCC, m_1 is the dry weight of the modified GCC, m_2 is the weight of ash, and α is the loss on ignition of GCC at 575℃ for 4h. The utilization rate of the complexes which were composed of starch, sodium stearate, and sodium hexametaphosphate, were calculated using Eq. 2,

$$Y(\%)=\frac{C}{M}\times 100 \tag{2}$$

where Y is the complex utilization rate, M is the total amount of complexes added to coated materials during the modification, and C is the coating weight (Fan *et al*. 2014).

Testing of paper optical properties and strength properties

Papers were put in ISO constant temperature and humidity chamber for 24 h. Tensile, burst, and tear strength were measured by L&W CE062 tensile testing apparatus (Sweden), L&W CE180 burst testing apparatus (Sweden), and L&W 009 tear testing apparatus (Sweden), respectively. Paper brightness and opacity were tested using a Testing Machine Inc. (TMI) MTCRO-TB-IC instrument (Sweden).

RESULTS AND DISCUSSION

Coating Weight and Utilization Rate

Effects of precipitation temperature on coating weight and the utilization rate

According to Table 1, the coating weight of modified GCC and the utilization rate were decreased when the precipitation temperature was raised from 40 °C to 90 °C. This was because the solubility of the starch was directly affected by the precipitation temperature during the final phase of modification. The higher precipitation temperature contributed to the higher solubility of starch, which was not conductive to increasing the coating weight. It was clear that a great change in the coating weight of modified GCC and the complex utilization rate appeared when the precipitation temperature was varied from 60 °C to 70 °C.

The maximum of the coating weight of modified GCC and the complex utilization rate was reached when the precipitation temperature was at 50 °C. The coating weight of modified GCC and the complex utilization rate were 24.93% and 97.76%, respectively, when the precipitation temperature was at 40 °C. The coating weight and the utilization rate reached a maximum of 25.0% and 98.0%, respectively when the precipitation temperature was at 50 °C. When the precipitation temperature was at 60 °C, the coating weight and the utilization rate were 25.0% and 97.7%, respectively. This showed that the coating weight of modified GCC and the complex utilization rate of 40 °C, 50 °C, and 60 °C were close, but all of them were much larger than the coating weight of modified GCC and the complex utilization rate of which the precipitation temperature was at 70 °C, 80 °C, and 90 °C. It could be concluded that the coating weight of modified GCC and the utilization rate would be improved at a lower precipitation temperature.

Table 1. Effect of Precipitation Temperature on the Coating Weight of Modified GCC and the Complex Utilization Rate

Precipitation temperature (°C)	40	50	60	70	80	90
Coating weight (%)	24.93	24.99	24.92	21.91	20.31	18.43
Utilization rate (%)	97.76	98.00	97.73	85.92	79.65	72.27

The level of the precipitation reaction temperature could directly affect the coating weight of modified GCC and the complex utilization rate. The differences of the coating weight of modified GCC and the complex utilization rate between 40 °C and 60 °C were tiny. In order to save the cooling time and decrease the production cost, 60 °C was judged to be the more suitable precipitation temperature. Starch is the main component of the complex; its dosage was reduced during the modification with the complex utilization or when the starch utilization rate was increased.

Effects of the dosage of sodium hexametaphosphate on coating weight and the utilization rate

As shown in Table 2, the coating weight of modified GCC increased with the increasing dosage of sodium hexametaphosphate. The maximum coating weight was 24.68%, which was about 8.29% higher than the coating weight of modified GCC without using hexametaphosphate. The increments of the coating weight of modified GCC were large when the dosage of sodium hexametaphosphate was varied from 1.0% to 1.5%. However, the increments of the coating weight of modified GCC were smaller when the dosage of sodium hexametaphosphate was varied from 1.5% to 3.0%. The maximum coating weight was increased only 0.23% in comparison to when hexametaphosphate was added at 1.5%. These results were attributed to the fact that the dissolved starch was further separated from water after sodium hexametaphosphate was added. Afterwards, the precipitated starch was further coated to the surface of modified GCC. In addition, sodium hexametaphosphate became part of modified GCC, and this also have contributed to the increase of the coating weight of modified GCC.

Table 2. Effect of the Dosage of Sodium Hexametaphosphate on the Coating Weight of Modified GCC and the Complex Utilization Rate

Dosage of sodium hexametaphosphate (%)	0	0.5	1．0	1.5	2.0	2.5	3.0
Coating weight (%)	16.39	20.23	21.71	24.45	23.54	24.68	24.51
Utilization rate (%)	68.29	82.57	86.84	95.88	90.55	93.13	90.78

The complex utilization rate increased when the dosage of sodium hexametaphosphate was increased from 0% to 1.5%. When the dosage of sodium hexametaphosphate was 1.5%, the complex utilization rate reached a maximum of 95.88%. The maximum increased by 27.6% in comparison to the complex utilization rate of which sodium hexametaphosphate was not added. That was because the sodium hexametaphosphate is cross-linking agent, and so it can increase the combination between modifiers and GCC. When the dosage of sodium hexametaphosphate was raised from 1.5% to 3.0%, the coating weight of the modified GCC increased, while the complex utilization rate indeed decreased. This was because the increment of the coating weight of modified GCC was smaller than the increment of the dosage of sodium hexametaphosphate. The sodium hexametaphosphate did not adequately react to become a part of the coated film. Some of the sodium hexametaphosphate remained dissolved in water on account of its good solubility. It was demonstrated that a proper dosage of sodium hexametaphosphate could greatly increase the coating weight of modified GCC and the complex utilization rate.

Effects of Modified GCC on Optical Properties and Strength Properties of Paper

Papers filled with modified GCC and unmodified GCC were formed by the Manual Sheet Former. Figures 1 through 5 document the effects of modified GCC filler on the optical properties and strength properties of the paper.

Effects of modified GCC on the optical properties of paper

As shown in Figs. 1 and 2, compared with the brightness (81.3%) and opacity (71.5%) of unfilled paper, the brightness and opacity in the presence of unmodified GCC and modified GCC filled paper were remarkably improved. This was the internal light-scattering interface of the paper increased as filler added. Four kinds of interfaces exist within paper. These are fiber-fiber, fiber-air, fiber-filler, and filler-air. The presence of each of these types of interface can be expected to affect paper brightness and opacity. The brightness of unmodified GCC paper was higher than that of modified GCC paper due to the unmodified GCC's brightness (91.51%) being higher than the modified GCC's brightness (88.92%). Moreover, the specific surface area of unmodified GCC was about 6 times as big as modified GCC, which was beneficial to light scattering of unmodified GCC.

Figure 2 shows that the opacity of paper filled with either modified GCC or unmodified GCC was initially increased as the ash content increased. However, the opacity of paper made with modified GCC filled paper decreased markedly as the ash content increased beyond 30%. This can be explained by noting that the air-solid interfacial area is likely to increase with increasing levels of filler, as the particles tend to create spaces between the fibers of the paper. Afterwards, the level of mineral is high enough that the particles become mutually packed together, filling up the air spaces in the paper. Compared with unmodified GCC, the reduction degree of modified GCC filled paper opacity was more obvious. This was attributed to the ability of the starch on the modified GCC surfaces to deform and fill up air spaces efficiently. Therefore, the internal light contact area was greatly decreased. In addition, the light absorptivity of starch was stronger than that of the fiber.

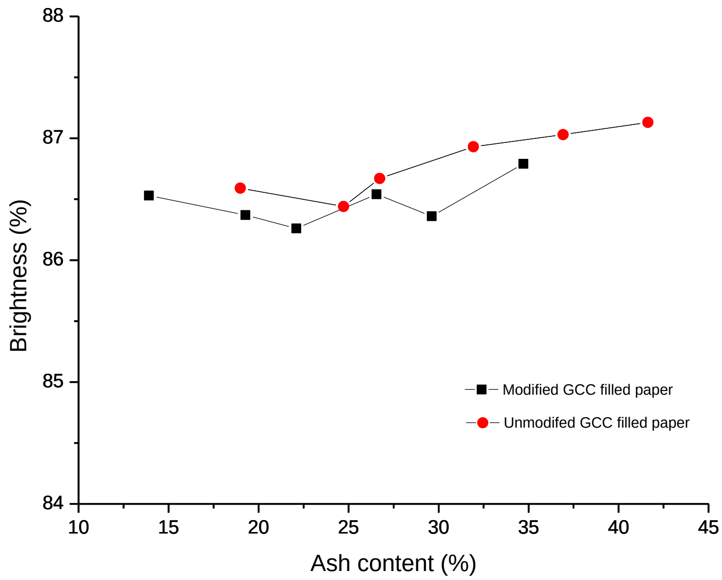

Fig. 1. Brightness of handsheets as a function of unmodified GCC and modified GCC with various ash contents

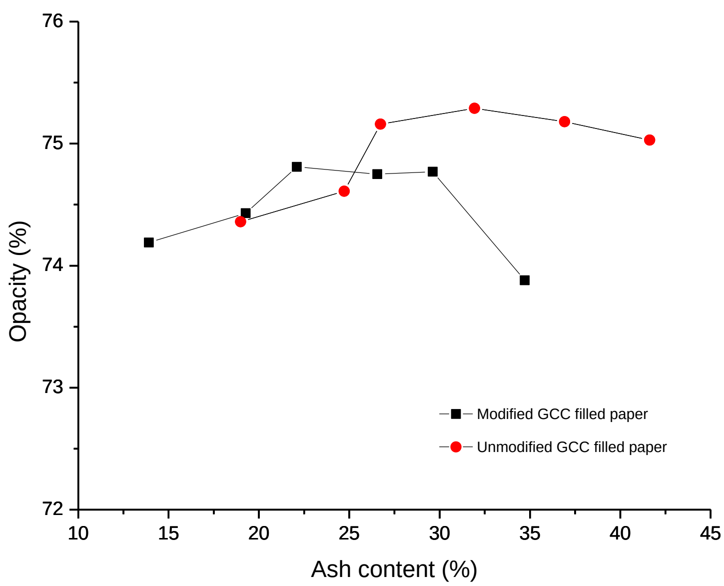

Fig. 2. Opacity of handsheets as a function of unmodified GCC and modified GCC with various ash contents

Effects of modified GCC on the strength properties of paper

Figures 3 to 5 show that the tensile, burst, and tear index of unmodified GCC filled paper were approximately linearly decreased as the filler content was increased. The tensile index of modified GCC was increased and then decreased when the ash content was raised from 13.9% to 19.3%. The tensile index in the case of modified GCC was noticeably higher than with unmodified GCC at the same ash content. The difference of tensile index between modified GCC and unmodified GCC was smallest when the ash content was about 27%, but compared with unmodified GCC, the tensile index of modified GCC still increased more than 25% at this ash content level.

The burst index of modified GCC increased and then decreased as the ash content increased. The burst index of modified GCC was markedly higher than that of unmodified GCC at the same ash content. The burst index decreased when ash content was 23%, that was due to the paper strength was affected by fillers' obstruction to fibers' bonding both of modified GCC filled papers and unmodified GCC filled papers. Compared with unmodified GCC, the burst index of modified GCC was increased by more than 70% when the ash content was about 23%.

The tear index of modified GCC increased, and then decreased as the ash content increased. The tear index of modified GCC was noticeably higher than that of unmodified GCC at the same ash content. The tear index of modified GCC reached the maximum of 3.61 kPa•m^2/g when the ash content was 22.10%, compared with the tear index of unmodified GCC filled paper at 22.10%, which increased more than 80%.

The tensile index, burst index, and tear index of modified GCC filled paper were dramatically higher than unmodified GCC filled paper at the same filler content. That was attributed to the ability of hydroxyl groups on starch to form hydrogen bonds with cellulose molecules, which made up for the loss of strength that usually would be expected upon the addition of filler.

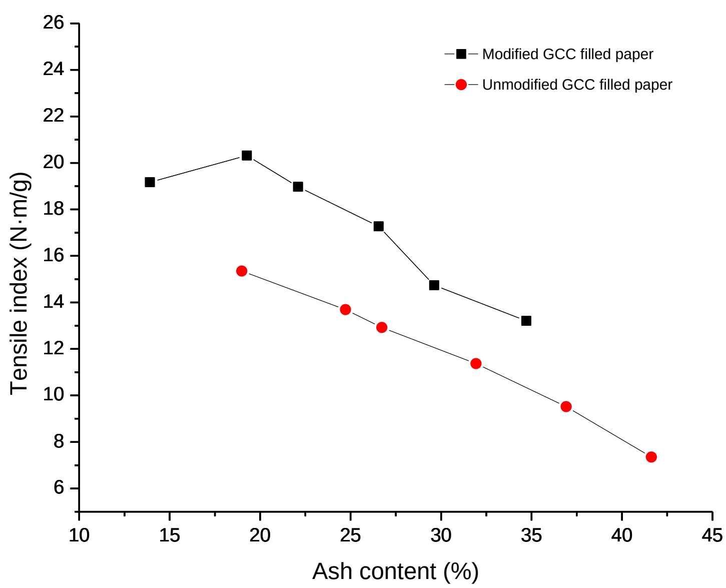

Fig. 3. Tensile index of handsheets as a function of unmodified GCC and modified GCC with various ash contents

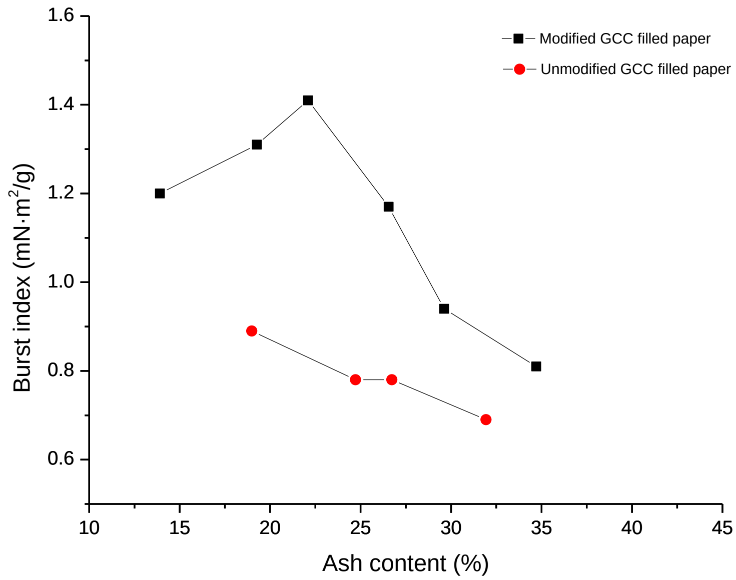

Fig. 4. Burst index of handsheets as a function of unmodified GCC and modified GCC with various ash contents

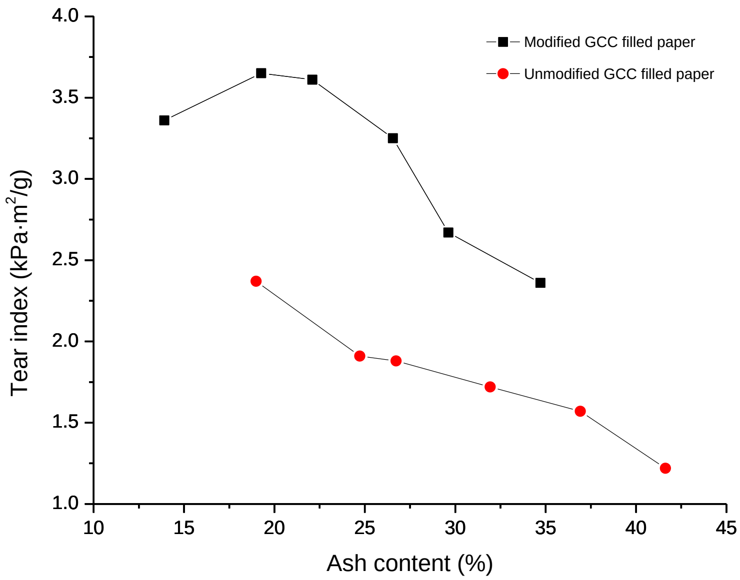

Fig. 5. Tear index of handsheets as a function of unmodified GCC and modified GCC with various ash contents

SEM Observations of Modified GCC and Unmodified GCC

From Fig. 6, it was found that the edge of modified GCC was smoother than unmodified GCC. This was attributed to coating with a layer of complex, which would reduce the angular sharpness. Furthermore, Fig. 6 intuitively shows that the bonding between modified GCC and fibers were closer than unmodified GCC. This is due to the fact that starch on the surface of modified GCC complex had a high content of hydroxyl functions, which could engage in hydrogen bonding with fibers, and then improve the paper strength.

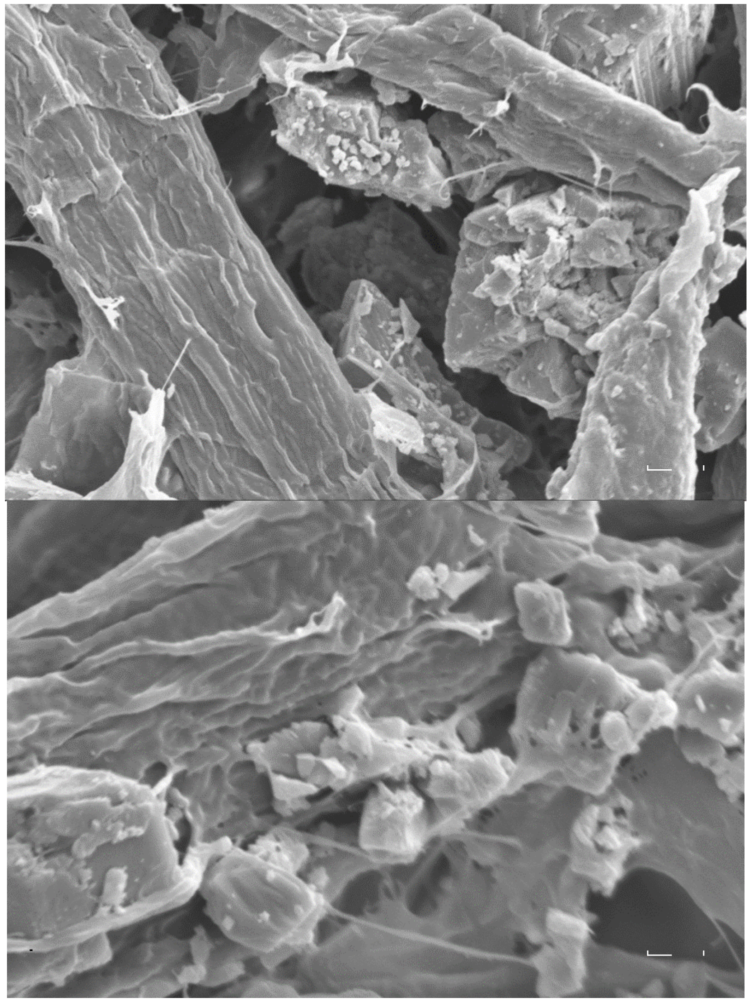

Fig. 6. SEM images of (a) unmodified GCC and (b) modified GCC

CONCLUSIONS

1. The lower precipitation temperature was contributed to the higher coating weight of modified GCC and the higher complex utilization rate. The suitable precipitation temperature was 60 ˚C
2. The coating weight of modified GCC was increased as the dosage of sodium hexametaphosphate was increased. The utilization rate reached the maximum when the dosage of sodium hexametaphosphate was 1.5%.
3. In terms of the paper strength properties, modified GCC filled paper performed better than unmodified GCC filled paper at the same ash content. In terms of the optical properties of paper, the brightness and opacity of unmodified GCC were better than those of modified GCC.

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REFERENCES CITED

Bai, W. R., and Fan, H. M. (2011). "Preparation of starch-stearic complex modified PCC filler and its application as paper filler," *China Pulp and Paper Industry* 30(1), 5-9.

Barhoum, A., Rahier, H., Abou-Zeid, R. E., Rehan, M., Dufour, T., Hill, G. T. H., and Dufresne, A. (2014). "Effect of cationic and anionic surfactants on application of calcium carbonate nanoparticles in paper coating," *ACS Applied Materials & Interfaces* 6(4), 3546-3557.

Beazley, K. M. (1993). *Papermaking Fillers-An Update*, Pira, Leather-head, UK.

El-Sherbiny, S., El-Sheikh, S. M., and Barhoum, A. (2015). "Preparation and modification of nano calcium carbonate filler from waste marble dust and commercial limestone for papermaking wet end application," *Powder Technology* 279(5), 290-300.

Fan, H. M., Wang, D. X., Bai, W. R., and Liu, J. A. (2012). "Starch-sodium stearate complex modified PCC filler and its application in papermaking," *BioResources* 7(3), 3317-3326. DOI: 10.15376/biores.7.3.3317-3326

Fan, H. M., Xu, B. F., Liu, J. A., and Zhang, C. (2014). "Effect of starch dosage on the properties of modified ground calcium carbonate," *BioResources* 9(3), 4679-4689. DOI: 10.15376/biores.9.3.4679-4689

Feng, C., Chen, G., Chai, X. S., and Fang, Z. Q. (2010). "Effect of calcium carbonate-fiber fines composite fillers on the paper properties," *China Pulp and Paper Industry* 29(2), 14-17.

Griggs, W. H. (1988). "Use of fillers in paper making," *TAPPI Journal* 71(2), 77-81.

Huang, X. J., Shen, J., and Qian, X. R. (2013). "Filler modification for papermaking with starch/oleic acid complexes with the aid of calcium ions," *Carbohydrate Polymers* 9(1), 931-935. DOI: 10.1016/j.carbpol.2013.07.024

Lu, Z. H., Li, M., and Liu, H. J. (2010). "Simple introduction of paper filler," *Journal of Hubei Papermaking* 4, 40-44.

Mabee, S. W. (2001). "Controlled filler preflocculation: Improved formation, strength and machine performance," *Proceedings of TAPPI Papermakers Conference*, Cincinnati, OH.

Mabee, S. W., and Harvey, R. (2000). "Filler flocculation technology-increasing sheet filler content without loss in strength or runnability parameters," *Proceedings of TAPPI Papermakers Conference*, Vancouver, BC, Canada.

Morsy, F. A., El-Sheikh, S. M., and Barhoum, A. (2014). "Nano-silica and $SiO_2/CaCO_3$ nanocomposite prepared from semi-burned rice straw ash as modified papermaking fillers," *Arabian Journal of Chemistry* 24(6), 1-11. DOI:10.1016/j.arabjc.2014.11.032

Ono, H., and Deng, Y. (1997). "Flocculation and retention of precipitated calcium carbonate by cationic polymeric microparticle flocculants," *Journal of Colloid and Interface Science* 188(1), 183-192. DOI: 10.1006/jcis.1997.4766

Sang, Y., McQuaid, M., and Englezos, P. (2012). "Pre-flocculation of precipitated calcium carbonate filler by cationic starch for highly filled mechanical grade paper," *BioResources* 7(1), 354-373. DOI: 10.15376/biores.7.1.354-373
Shen, J., Song, Z., and Qian, X. (2009). "Investigations on the preparation of starch/sodium oleate/alum modified precipitated calcium carbonate filler and its use in papermaking," *Appita Journal* 62(5), 360-364,382.
Shen, J., Song, Z., and Qian, X. (2009). "Modification of papermaking grade fillers: A brief review," *BioResources* 4(3), 1190-1209. DOI: 10.15376/biores.4.3.1190-1209
Song, D., Dong, C., Ragauskas, A., and Deng, Y. (2009). "Filler modification with polysaccharides or their derivatives for improved paper properties," *Journal of Biobased Materials and Bioenergy* 3(4), 321-334. DOI: 10.1166/jbmb.2009.1042
Wang, H. P., Zhang, G. H., Lai, Z. C., and Shen, Y. (2010). "Preparation of cationic starch modified GCC filler and its application in high-filler paper," *China Pulp and Paper Industry* 29(1), 6-8.
Wu, H. Y., and Zhang, H. W. (2010). "Preparation of coated GCC and its effects on the property of paper," *China Pulp and Paper Industry* 29(6), 24-27.
Yan, Z. G., Liu, Q. J., and Deng, Y. L., and Ragauskas, A. (2005). "Improvement of paper strength with starch modified clay," *Journal of Applied Polymer Science* 97(1), 44-50. DOI: 10.1002/app.21727
Yong, S. Y., and Deng, Y. (2006). "Starch-fatty complex modified filler for papermaking," *TAPPI Journal* 5(9), 3-9.
Zhang, G. H., Wang, H. P., Wang, X. X., Lai, Z. C., and Li, W. (2010). "Preparation and application of composite filler based on AKD-starch- calcium carbonate," *China Adhesives* 19(1), 35-39.
Zhao, Y., Hu, Z., Ragauskas, A. J., and Deng, Y. (2005). "Improvement of paper properties using starch-modified precipitated calcium carbonate filler," *TAPPI Journal* 4(2), 3-7.
Zhu, H. L., Chen, K. F., and Chen, G. (2007). "Modification and application technology of filler used in paper industry," *Papermaking Science and Technology* 26(5), 46-48.

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