Effect of Starch Dosage on the Properties of Modified Ground Calcium Carbonate

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Ground calcium carbonate (GCC) was modified with a starch/sodium stearate complex and used to prepare different coating weights by controlling the starch dosages. Modified GCC was characterized by scanning electron microscopy (SEM) and particle size analysis. The effects of starch dosage (based on the dry weight of GCC) on the size of modified GCC, the coating weight of modified GCC, and the utilization rate of starch were evaluated. Four kinds of modified GCC with different coating weights obtained by controlling the starch dosage were studied in the last part of this paper. The starch dosage was found to play an important role in the coating weight of starch/sodium stearate complex used in preparing the modified GCC and the utilization rate of starch, but did not have as much of an effect on the size of modified GCC. The higher coating weight was beneficial for retention of the filler retention and for enhancing paper strength properties at the same ash content. The higher coating weight, however, caused a decrease in the paper ash content at the same initial added filler.

Keywords: Starch/sodium stearate complexes; Modified GCC; Ash; Strength; Coating weight; Utilization; Size; Retention

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INTRODUCTION

In the paper industry, adding mineral fillers such as kaolin clay and calcium carbonate is a well-established practice to reduce the cost and energy of papermaking (Cheng *et al*. 2011; Dong *et al*. 2008). Another benefit associated with the use of mineral fillers is that many critical properties of traditional paper, such as optical properties, printability, and dimensional stability, can be improved remarkably (Huang *et al*. 2013; Lu *et al*. 2010; Shen *et al*. 2008).

However, the use of conventional mineral fillers, especially at high addition levels, leads to the decline of paper strength due to its interference with fiber-fiber bonding (Han 2009; Shen *et al.* 2009; Koivunen *et al.* 2010). Another challenge associated with the use of fillers is the difficulty of filler retention, particularly at high initial added filler. Chemical additives are needed to make up for the loss in strength and improve the retention, which is not always effective at high loading levels (Fan *et al.* 2012).

In recent years, filler surface modification as a valid approach to solve the problems mentioned above has attracted considerable interest (Deng *et al.* 2010; Yan *et al.* 2005; Yoon and Deng 2006; Zhao *et al*. 2005). Various polysaccharides and their derivatives, such as starch and chitosan, can be used as filler surface modifier to ameliorate the negative effect of filler addition on paper strength as well as improve filler retention (Bai and Fan 2011; Fatehi *et al.* 2013; Ghasemian *et al.* 2012). It has been reported that starch/sodium stearate complexes can be anchored on precipitated calcium carbonate (PCC) to ameliorate the performance of PCC, taking advantage of the gelatinized starch's bonding ability and the diadochy of sodium and calcium ions (Bai *et al*. 2012; Zhang 2013).

Starch as the primary modifier should be taken much more into account. The effect of starch dosage (based on the dry weight of GCC) on the size of modified GCC, the coating weight of starch/sodium stearate complex used in modification of the GCC, the utilization rate of starch, the retention efficiency of modified GCC, and the improvement in paper strength properties was investigated in this study. The utilization rate of starch was introduced to depict the percentage of starch/sodium stearate complex on modified GCC.

EXPERIMENTAL

Materials

Ground calcium carbonate (GCC) was obtained from Guangning Zhongsheng Co., Ltd., China. Unmodified corn starch was provided by Shenzhen Taigang Food Co., Ltd., China. Sodium stearate was supplied by China Yuanhang Reagent Factory, China. Bleached eucalyptus pulp was a commercial pulp with a drainage degree of 32 °SR.

Methods

Preparation of starch-sodium stearate complex modified GCC

A 3.0% corn starch suspension was dispersed in cool water for 10 min under stirring at 400 rpm and then heated to 95 °C for 30 min. After this, sodium stearate complex was added to the gelatinized starch by stirring at 150 rpm for another 30 min. Afterwards, a 30% solid GCC slurry was poured into the starch-sodium stearate complex, and the mixture was dispersed with stirring at 500 rpm at 70 °C for 20 min. Then, the modified GCC with specified coating weights was obtained. The starch dosage was varied from 12.5% to 100% (based on the dry weight of GCC).

SEM observations of filler

Dried samples of GCC and modified GCC were mounted on aluminum stubs with tape and sputter-coated with a gold alloy. Samples were observed using an EVO 18 Special Edition scanning electron microscopy (Carl Zeiss, Germany) operating at an accelerating voltage of 10.00 kV.

Modified GCC size measurement

GCC and modified GCC were diluted and dispersed in deionized water and the sizes were measured by a Malvern Mastersizer 2000 (Malvern Instruments Ltd., UK). Every sample was tested four times and averaged.

Evaluation of coating weight of modified GCC

A certain constant-weight modified GCC and GCC was incinerated at 575 °C for 4 h or more until to be a constant weight and the ash weight was calculated. The starch coating weight can be expressed as the percentage of starch/sodium stearate complex in modified GCC and calculated with Eq. 1,

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

where C is the coating weight of starch/sodium stearate complex on mineral, m_1 is the constant-weight of the modified GCC, m_2 is the constant-weight of ash, and α is the loss on ignition of GCC at 575 °C for 4 h or more.

Estimation of the utilization of starch

The utilization rate of starch was introduced to measure the effect of starch dosage on the coating weight and calculated using Eq. 2,

$$Y(\%) = \frac{C}{A} \times 100, \quad A(\%) = \frac{m_3}{m_4} \times 100 \qquad (2)$$

where Y is the utilization rate of starch, A is the amount of initial added starch, C is the coating weight, m_3 is the weight of starch, and m_4 is the weight of initially added GCC.

Handsheet preparation and determination of paper properties

The pulp was diluted to 0.3%, and various amounts of modified GCC were added during handsheet making. After the addition of filler, diluted cationic poly-acrylamide (CPAM) was added at 0.05 wt% (based on dry fiber) for filler retention under stirring for 5 min. Handsheets were formed using a Rapid-Köthen Sheet former (RK3-KWTjul; PTI Ltd., Austria) at a basis weight of approximately 72 g/m^2.

Papers were suspended in ISO constant temperature and humidity chamber for 12 h. Then, tensile, burst, and tear strength were measured using an L&W CE062 tensile testing apparatus, L&W CE180 burst testing apparatus, and L&W 009 tear testing apparatus (Lorentzen & Wettre, Sweden).

Retention efficiency of modified GCC

Handsheets filled with modified GCC and GCC were incinerated at 575 °C for 4 h or more until to be a constant weight and the ash was weighed. Filler retention was calculated using Eq. 3,

$$R_1(\%) = \frac{m_6(1+C)}{m_5(1-a)} \times 100 \quad R_2(\%) = \frac{m_6}{m_5(1-a)} \times 100, \qquad (3)$$

where R_1 is the retention efficiency of modified GCC, R_2 is the retention efficiency of GCC, m_6 is the weight of ash, m_5 is the dry weight of filler added to paper (GCC or modified GCC), and a is the loss on ignition of GCC at 575 °C for 4 h or more.

RESULTS AND DISCUSSION

Characterization of Modified GCC

The effect of starch dosage on properties of modified GCC, such as the coating weight, the utilization rate of starch, and the size of modified GCC, was investigated.

SEM observations of modified GCC

As shown from SEM images (Fig. 1), the surface morphology of modified GCC was substantially different from that of unmodified GCC, indicating that GCC was readily coated by the starch/sodium stearate complex. It can also be seen that the modification of GCC resulted in some kind of aggregation of GCC particles, which was beneficial to lower the abrasiveness and to improve the efficiency of filler retention (Mabee and Harvey 2000).

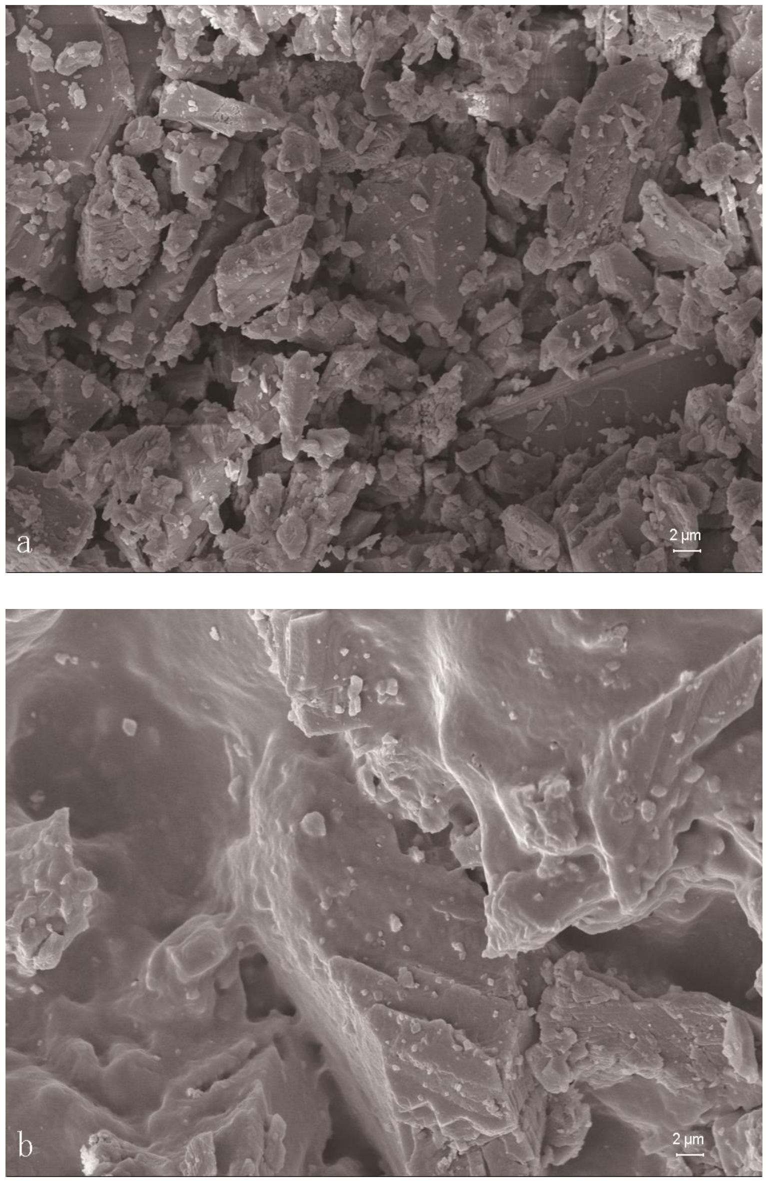


Fig. 1. (a) SEM images of (a) GCC and (b) modified GCC. Starch dosage, 25% and sodium stearate, 3% (based on the dry weight of GCC)

Size of modified GCC

As shown in Fig. 4, the size of modified GCC particles increased from 32.8 µm to 36.2 µm when the starch dosage was varied from 12.5% to 100%. The size of modified GCC (32.8 to 36.2 µm) was approximately two to three times larger than the size of unmodified GCC (14.8 μm), demonstrating that some kind of aggregations of GCC particles were formed with the aid of starch/sodium stearate complex. Moreover, the biggest particle of modified GCC was only 3.4 μm larger than the smallest one, indicating that the starch dosage also had influence on the size of modified GCC, but not too much.

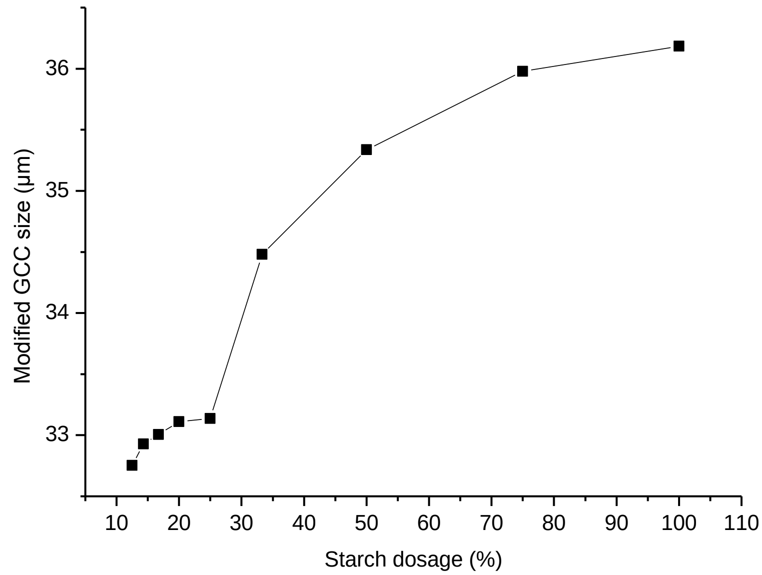


Fig. 2. Relationship between modified GCC sizes and starch dosage

Coating weight and the utilization rate of starch

It was clear that the coating weight increased linearly with the augment of starch dosage, as shown in Fig. 3. It also can be found that the coating weight was close to the starch dosage. For instance, the coating weight was 8.55% when the starch dosage was 12.5%, and it increased to 95.78% when the starch dosage was 100%.

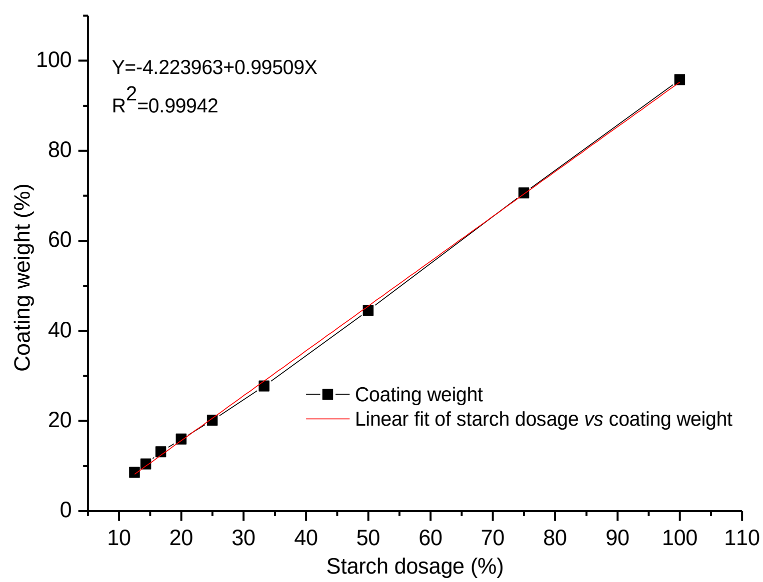


Fig. 3. Relationship between the coating weight and starch dosage (based on the dry weight of GCC)

As shown in Fig. 4, the utilization rate of starch was increasing with the increase of starch dosage. The utilization rate of starch was only 68.4% when the starch dosage was 12.5% and increased to 95.78% when the starch dosage was 100%. This observation showed that the more starch/sodium stearate complex coated on GCC, the easier it was for modified GCC to precipitate more starch/sodium stearate complex on it. This was because the starch/sodium stearate complex had precipitated on GCC could form hydrogen bonds with the starch/sodium stearate complex that had not precipitated on GCC. And the more starch/sodium stearate complex coated on GCC, the more hydrogen bonds can be formed.

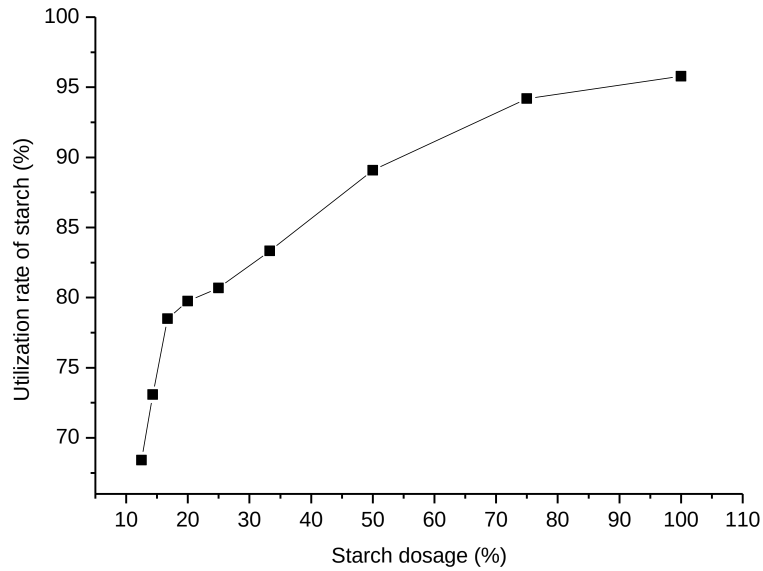


Fig. 4. Relationship between utilization of starch and starch dosage (based on the dry weight of GCC)

Use of Modified GCC in Papermaking

Four modified GCCs with coating weights of 8.55%, 20.17%, 27.75%, and 95.78% and unmodified GCC were chosen to be used in filled paper with various initial added fillers. The effect of the coating weight on filler retention and the ash content was shown in Figs. 5 and 6, and the effects on paper tensile index, bursting index, and tearing index are shown in Fig. 7.

Retention of fillers and ash content

As shown in Fig. 5, the retentions of modified GCCs were all higher than the retention of unmodified GCC. This was mainly because the modified GCC formed by the aggregation of GCC particles was more easily filtered by the mat of fibers. Also, the hydrophobic stearate “tails” in starch/sodium stearate complex can provide a driving force for the modified GCC to come out of solution and to deposit onto cellulosic surfaces. It can also be seen that the retention of modified GCC with higher coating weight was higher than the one with lower coating weight at the same initial added fillers. For example, when 15% filler was added, the retention of the 95.78% coating weight modified GCC was 73.56%, which was approximately 7% higher than the 20.17% coating weight modified GGC and 11.5% higher than the 8.55% coating weight modified

GCC. This also indirectly indicated that the starch dosage played an important role in modified GCC retention.

As shown in Fig. 6, the paper filled with the higher coating weight modified GCC usually had lesser ash content at the same loading level. For example, when 15% filler was added, the ash content of the paper filled with the 95.78% coating weight modified GCC was only 9.25%, while the ash content of the paper filled with the 8.55% coating weight modified GCC was 15.81%. It is worth mentioning that the ash content of paper filled with unmodified GCC was very close to the ash content of the paper filled with the 27.75% coating weight modified GCC and was higher than the ash content of the paper filled with the 95.78% coating weight modified GCC. In addition, it is worth noting that the higher coating weight was beneficial to the modified GCC retention (Fig. 5), but also caused a decrease in paper ash content at the same loading levels (Fig. 6). This was because the percentage of starch coated on the GCC played an important role in the weight of modified GCC. For instance, when the starch dosage was 100%, the coating weight of modified GCC was 95.78%, which meant that starch/sodium stearate complex made up about 50% percent of modified GCC.

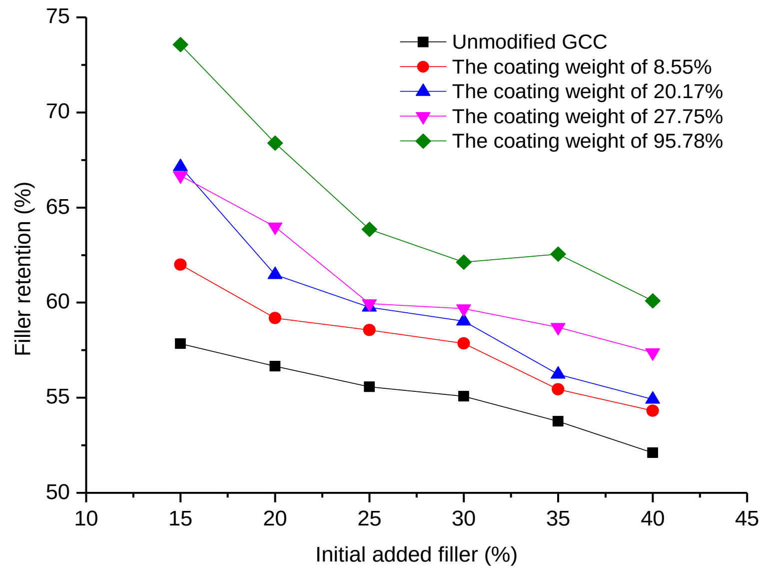


Fig. 5. Relationship between filler retention with different coating weights

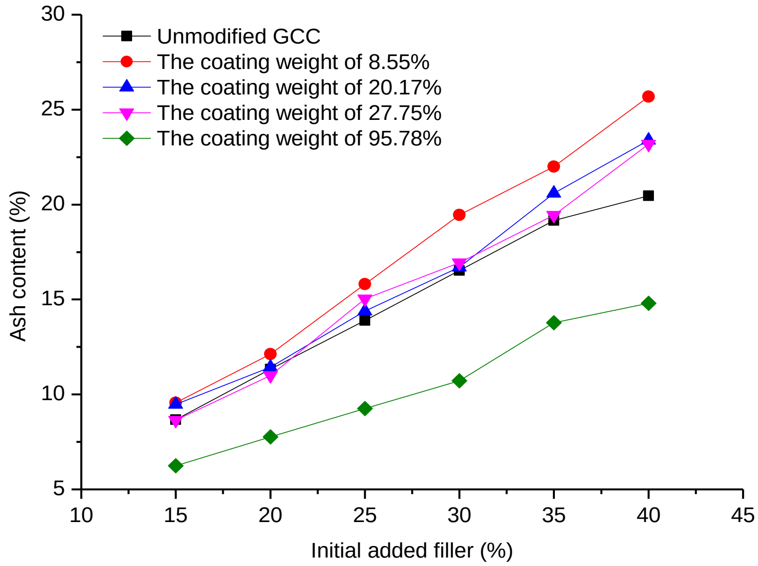
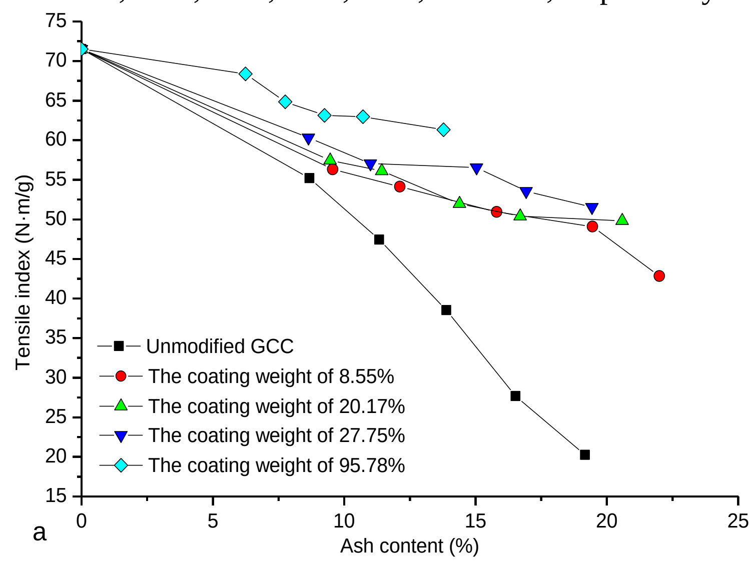


Fig. 6. Relationship between ash content and initial added filler

Effects of the modified GCC on paper strength properties

Modified GCCs with coating weights of 8.55%, 20.17%, 27.75%, and 95.78%, which were obtained by controlling starch dosages, were used in filled paper with initial added filler contents of 15%, 20%, 25%, 30%, 35%, and 40%, respectively.



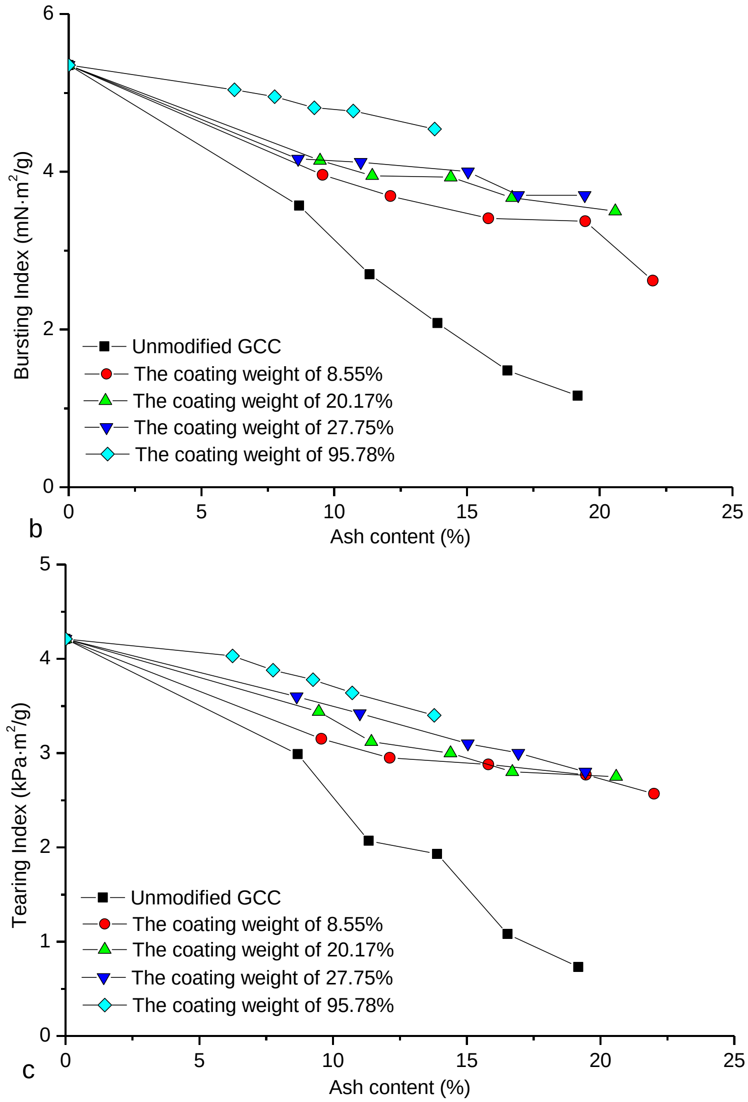


Fig. 7. (a) Tensile index as a function of filler content in paper for different coating weights; (b) burst index as a function of filler content in paper for different coating weights; and (c) tear index as a function of filler content in paper for different coating weights

As illustrated in Fig. 7, the physical strength of paper filled with modified GCC was always higher than the paper filled with unmodified GCC at the same ash content (Fig.7). The physical strength of the paper filled with high coating weights was higher than that of the paper filled with low coating weights at the same ash content. For instance, at ash content of 10%, compared with the paper filled with the 8.55% coating weight, the paper filled with the 95.78% coating weight was about 12% higher in tensile index, 25% higher in bursting index, and 18% higher in tearing index. This was because the more starch/sodium stearate complex coated on GCC, the more hydrogen bonds and covalent bonds formed with fibers, which could minimize the interference on fiber-fiber bonding caused by the filler addition (Shilin *et al.* 2011). Additionally, it is worth mentioning that the properties of papers filled with modified GCC with coating weights of 20.17% and 27.75% were close in tensile index, burst index, and tear index. This showed that the coating weight plays an important part in the properties of modified GCC.

Finally, these results indicated indirectly that the starch dosage play an important part in the property of modified GCC.

CONCLUSIONS

1. The surface morphology of modified GCC was substantially different from unmodified GCC for the encapsulation of starch/sodium stearate complex.
2. The size of modified GCC was mainly dependent on how many GCC particles were attached together. The starch dosage also played a role in the size of modified GCC, but not too much.
3. The coating weight of starch/starch sodium state complex on $CaCO_3$ increased linearly with the augment of starch dosage. And the coating weight played a very important role in the retention of modified GCC and paper strength.
4. The higher coating weight was beneficial to the retention of modified GCC, but also caused a decrease in paper ash content at the same initial added filler; however, a high coating weight was a detriment to increasing the ash content of filled paper.
5. Papers filled with modified GCC with high coating weight had higher physical strength than papers filled with low coating weight.

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