Effect of Hydrodynamic Shear on Agglomerated Ground Calcium Carbonate Filler after Surface Modification with Starch and its Effects on Paper Properties

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Ground calcium carbonate (GCC) was modified with starch, sodium stearate, and sodium hexametaphosphate prior to the papermaking process. This paper is focused on the effect of shear on the modified GCC and considers the impact of adding modified GCC into paper. The coating efficiency of starch on GCC was investigated in terms of the shear-tolerance of the agglomerated filler. Experimental results showed that the precipitation temperature and the amount of crosslinking agent, sodium hexametaphosphate, both were important relative to shear tolerance. Lower precipitation temperature was beneficial for the starch coating. Within a certain range, more sodium hexametaphosphate led to a stronger complex. The results showed that 1.5% (based on M_{GCC}) of sodium hexametaphosphate and a precipitation temperature of 60 °C were the optimum conditions for shear tolerance.

Keywords: Starch/sodium stearate complexes; Modified GCC; Shear tolerance; Properties of paper

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INTRODUCTION

In the paper industry, filler is the second most commonly used raw material after wood fibers. Many kinds of mineral fillers have been used in the papermaking industry, such as kaolin clay, talc, titanium dioxide, and calcium carbonate. Calcium carbonate is commonly applied to improve whiteness and reduce papermaking cost. When filler is added into the paper, it improves the brightness, opacity, and smoothness. It also reduces moisture absorption and degree of deformation of the paper (Li *et al*. 2007; Fan *et al*. 2014). Since the use of filler could reduce production costs and energy needs, it is an active field of research (Deng *et al.* 2010). As reported, filler use for newsprint, package board, and tissue paper has become a growing area of interest (Zhao *et al.* 2008; Deng *et al.* 2010). However, some strength properties of paper such as tensile, burst, and tear strength are usually decreased because of filler addition. That could be explained by the fact that, to some extent, fillers interrupt fiber-fiber bonding interactions, thus degrading the physical properties of paper (Koivunen *et al.* 2010; Xie *et al*. 2010).

Many approaches have been used in an attempt to solve the problems caused by filler addition, including modifications of milling (Christidis *et al.* 2004), preflocculation (Ono and Deng 1997; Mabee *et al.* 2000), synthesis of filler with different structures and functions (Enomae and Tsujino 2004), surface medication (Yan *et al.* 2005; Zhao *et al.* 2005; Yoon *et al.* 2006; Deng *et al.* 2008), lumen loading (Zakaria *et al.* 2004; Yoon *et al.* 2007), and using composite filler. In the current study, the use of mineral filler modified *via* polysaccharides and their derivatives is used as a valid approach to handle the problems associated with fillers (Yan *et al*. 2005; Zhao *et al*. 2005; Yoon and Deng 2006; Deng *et al*. 2008). It is known that the use of starch gel coating has the benefits of maintaining paper strength and increasing filler loading.

In this paper, starch and GCC were added to form a slurry first. Modified GCC was then obtained by adding the hydrophobic agent, sodium stearate, and crosslinking agent, sodium hexametaphosphate, during the heating process. It is proposed that starch and lipid compounds form a hydrophobic starch-lipid complex by means of an ester bond, adsorption, or mechanical association under certain conditions. It is further proposed that two or more reactive groups of hexametaphosphate interact with the hydroxyl groups of the starch, resulting in crosslinking among starch molecules. This study mainly focused on the analysis of shear tolerance of the starch-coated GCC. The influence of precipitation temperature and the amount of hexametaphosphate on shear tolerance was also investigated. Furthermore, the quality of the coating performance was measured by testing the strength properties of paper when modified GCC was added.

EXPERIMENTAL

Materials

Bleached eucalyptus pulp with a drainage degree of 32 °SR was supplied by Henan Tianbang Co., Ltd. (China). The ground calcium carbonate (GCC) was provided by Guangning Paper Co., Ltd. (China), and corn starch by Guangdong Shenzhen Taigang Food Co., Ltd. (China). Sodium stearate, cationic polyacrylamide (CPAM), and cationic starch were all purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (China).

Methods

Modified GCC preparation

Deionized water was added to a mixture of starch and GCC (1:5 w/w) to form a GCC slurry with a concentration of about 15% (based on M_{GCC}, the mass of GCC was noted as M_{GCC}). The mixture was dispersed for 10 min. It was then cooked in a water bath at 95 °C and stirred at 200 rpm. After stirring for 50 min at 95 °C, 4.0% of sodium stearate (based on M_{GCC}) was added to the mixture, and stirred for another 30 min, followed by cooling to a temperature of either 40, 50, 60, 70, 80, or 90 °C. When cooled to the appropriate temperature, sodium hexametaphosphate solution (0, 0.5, 1.0, 1.5, 2.0, and 3.0% solutions based on the M_{GCC}) was added into the reaction mixture and stirred at 200 rpm for 30 min. The modified GCC was dried in a SX muffler oven (Zhongyuan Chemistry Instruments, China) at 105 °C for 4 h.

Paper preparation

The bleached eucalyptus pulp was diluted to 0.3% using tap water, and various concentrations (percent) of modified GCC (based on slurry) were added during handsheet making. The mixture was dispersed by a GBJ-A fiber standard disintegrator (Zhongyuan, China), and 0.05% CPAM (based on dry pulp) was added as a retention aid. The hand sheets were formed using a Rapid-Köthen Sheet former (RK3-KWTjul; PTI Ltd., Austria) at a basis weight of approximately 72 g/m^2.

Characterization of paper

Handsheets were placed in an ISO constant temperature and humidity chamber for 24 h (23 ± 1 °C, 50 ± 2% RH). The tensile, burst, and tear strength values of the papers were measured using an L&W CE062 tensile testing apparatus, an L&W CE180 burst testing apparatus, and an L&W 009 tear testing apparatus (Lorentzen and Wettre, Sweden), respectively.

RESULTS AND DISCUSSION

Analysis of the Effect of Hydrodynamic Shear on Modified GCC

As shown Fig. 1, the particle size of the modified GCC was invariable with respect to shear time at the constant precipitation temperature when the same amount of sodium hexametaphosphate was used, with a shear rate of 1000 rpm and 2000 rpm (shear time varies from 0 to 120 min). This indicated that modified GCC was well coated. When the GCC was stirred at 3000 rpm (120 to 180 min), the particle size of the modified GCC was significantly reduced, because a small portion of the composite was dispersed in water under shear force. However, the particle size of modified GCC increased rapidly when the shearing time was more than 140 min and was much larger than that of modified GCC (before 110 min). The modified GCC particles were held together by means of the adsorbed starch, as affected by its interactions with sodium hexametaphosphate. The results suggested that the effect of shear rate on particle size can be used effectively to evaluate shear-tolerance of the treated GCC and its state of agglomeration.

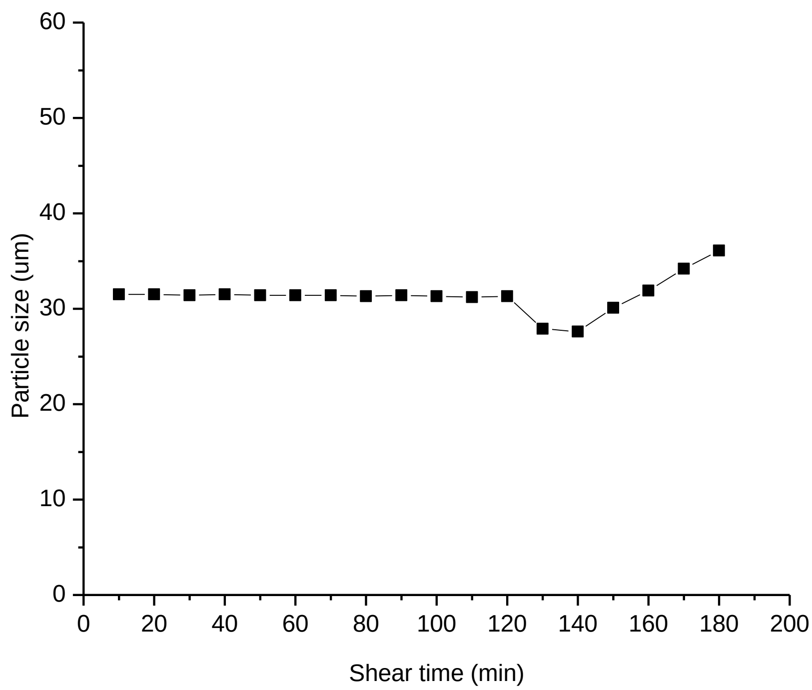

Fig. 1. Particle size as a function of shear time

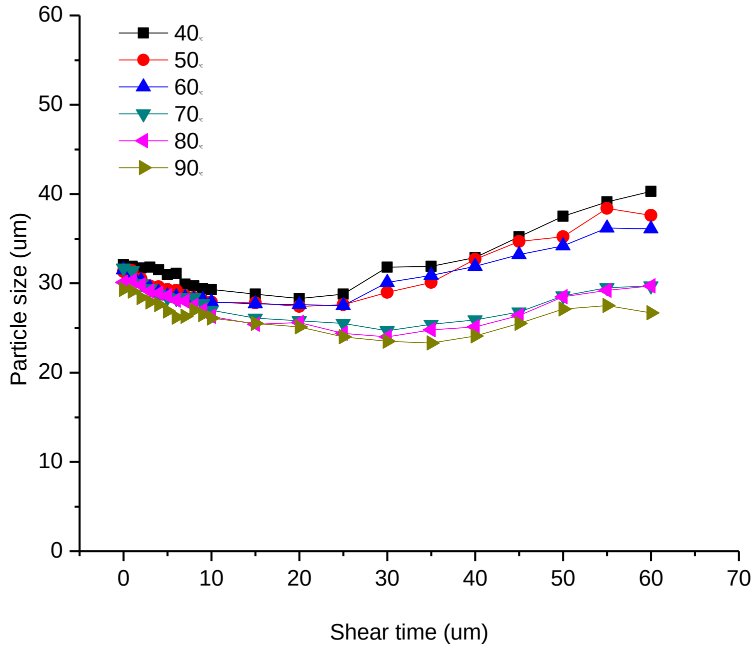

Fig. 2. Particle size as a function of precipitation temperature

As can be seen in Fig. 2, with the increase in shearing time, the particle size of the modified GCC decreased first and then increased, because a small portion of composite was peeled off from the surface of the agglomerated GCC as a result of the shearing force. With continued shearing, the shed starch became re-adhered to the modified GCC surface as a result of molecular motions and collisions. This may also occur due to collision and flocculation between the particles of the modified GCC. Modified GCC obtained at the precipitation temperatures of 40, 50, and 60 °C showed an increase in particle size compared to that of modified GCC at precipitation temperatures of 70, 80, and 90 °C.

When the shearing time was more than 25 min, the particle size was increased more apparently. This might be explained by the fact that the precipitation temperature has an impact on the nature of the coating film of the modified GCC during the preparation process. The lower the precipitation temperatures were, the better the starch and other substances precipitated from water and were coated on the GCC surface, such that they were more easily incorporated as a solid coating film. The nature of coated film had a certain influence on post-collision and flocculation. In addition, one can also find that at a higher precipitation temperature, the particle size decreased rapidly. Differences in the ability to withstand hydrodynamic shear by the modified GCC obtained at precipitation temperatures of 40, 50, and 60 °C were not very obvious. Considering the cost factor, the precipitation temperature of 60 °C was chosen to achieve the desired results.

Figure 3 shows the particle size of the modified GCC with respect to the amount of sodium hexametaphosphate used. The particle size decreased first and then increased when more sodium hexametaphosphate was used. However, without the addition of sodium hexametaphosphate (at 0%) into GCC, particle size was small, indicating that hexametaphosphate had a significant impact on the coated film of modified GCC. With the increase of the amount of sodium hexametaphosphate, modified GCC size increased. At 0.5%, 1.0%, 1.5%, 2.0%, and 3.0% of hexametaphosphate, the shearing times at which the particle size increased were, respectively, 40 min, 30 min, 25 min, 20 min, and 10 min.

This is because the more sodium hexametaphosphate there was, the easier it was to precipitate the starch from the water. Moreover, sodium hexametaphosphate had the advantage of strengthening the shear tolerance of the complex and reducing the rate of starch dissolution in water. It was also found that the treatment levels 1.5%, 2.0%, 3.0% of sodium hexametaphosphate resulted in the similar characteristics, which indicated that their coating performance was no different. Considering the cost, the concentration of the cross-linking agent, sodium hexametaphosphate was kept at 1.5%.

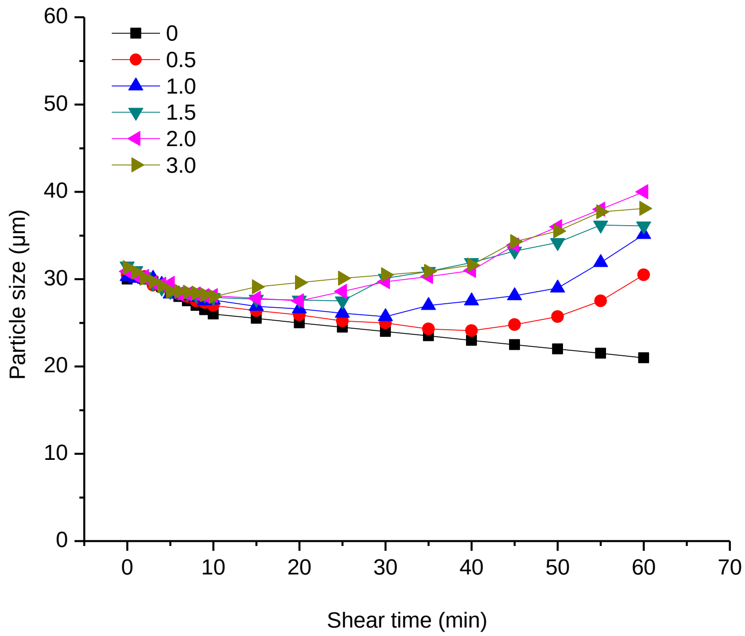

Fig. 3. Particle size as a function of the amount of sodium hexametaphosphate

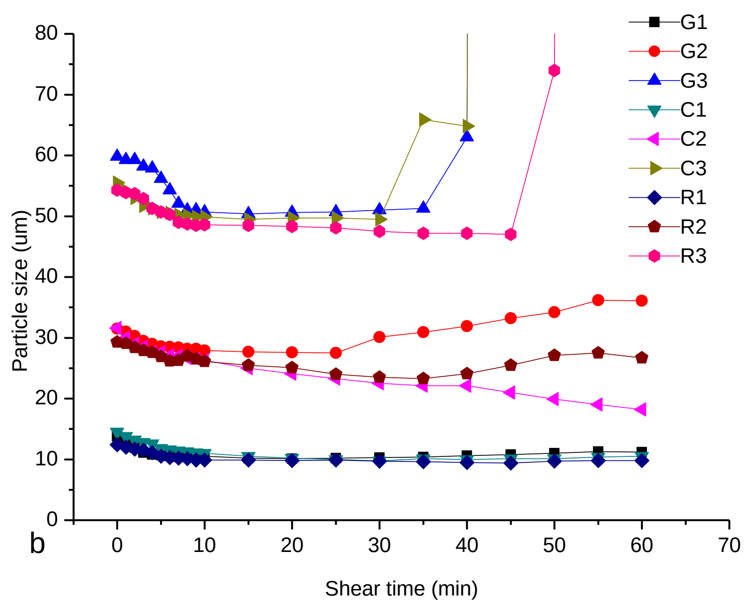

Fig. 4. Particle size as a function of shear time: G1) The minimum particle size in 60 ℃ & 1.5%; G2) The average particle size in 60 ℃ & 1.5%; G3) The maximum particle size in 60 ℃ & 1.5%; C1) The minimum particle size in 60 ℃ & 0.0%; C2) The average particle size in 60 ℃ & 0.0%; C3) The maximum particle size in 60 ℃ & 0.0%; R1) The minimum particle size in 90 ℃ & 1.5%; R2) The average particle size in 90 ℃ & 1.5%; R3) The maximum particle size in 90 ℃ & 1.5%

As can be seen in Fig. 4, G1, C1, and R1 were almost the same during the shearing process, but G2, C2, and R2 were different. G3, C3, and R3 showed a sudden surge when shearing times were 35, 30, and 45 min respectively, indicating that strong flocculation occurred during the shearing of modified GCC, and a larger particle size (> 100μm) was observed. Because the modified GCC complex moved strongly, multiple pieces of modified GCC were combined and turned into the larger modified GCC as a result of the violent collision.

From Fig. 5, when the shearing time of modified GCC was less than 10 min, which was achieved under the conditions for modified GCC: 60 °C and 1.5%, a crest existed in the region of 10 to 100 μm in the particle size distribution curve. When modified GCC was sheared for 20 min, a peak in the region of more than 1000 μm emerged in the particle size distribution curve. This peak was relatively lower, while the peak in the region of 10 to 100 μm was slightly shorter. With the increase of the shearing time, the peak in the region of 10 to 100 μm gradually became smaller; at the same time, the peak in the region of over 1000 μm gradually increased. This indicated that the amount of modified GCC in the region of 10 to 100 μm gradually decreased, while the amount of modified GCC in the region of more than 1000 μm increased the whole time. This can be explained by the observation that with the increase in shearing time, the movement of modified GCC was more intense with stronger collisions that led to flocculation. The flocculation was strengthened with continuous shearing action.

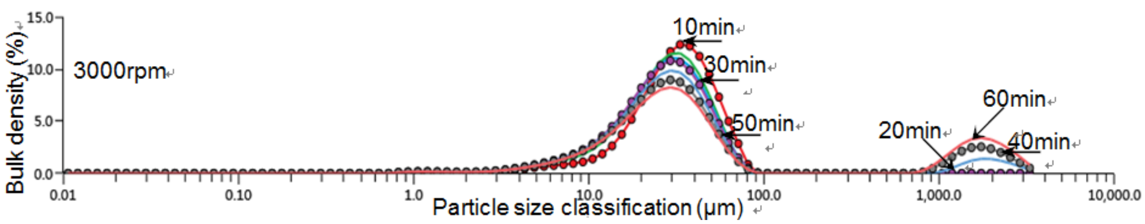

Fig. 5. Particle size and distribution as a function of shear time

Analysis of the Strength Properties of Paper

As shown in Fig. 6, the tensile strength of paper with unmodified GCC was reduced with an increase in ash content; however, the tensile strength of paper with modified GCC (reaction conditions were 60 °C and 1.5%, following the same procedures) was increased in the initial stage and then was reduced with an increase in ash content. At the same ash content, the tensile index of paper with modified GCC was higher than that of paper with unmodified GCC. When the ash content was about 27%, the gap between paper with modified GCC and unmodified GCC was small, and the tensile index of paper with modified GCC was at least 25% higher than that of paper with unmodified GCC. Moreover, when the ash content was about 20%, the tensile index of paper with modified GCC was at least 30% higher than that of paper with unmodified GCC. When the ash content went from 20% to 35%, the tensile index of paper with modified GCC was at 25% higher than that of paper with unmodified GCC. It can be found that when the ash content was about 29.7%, the tensile index of paper with modified GCC (14.7 N•m/g) was slightly higher than that of unmodified GCC (15.4 N•m/g) when the ash content was about 19.0%. This indicated that in filler paper, the ash content of paper with modified GCC was higher than that of unmodified GCC when their tensile index was the same.

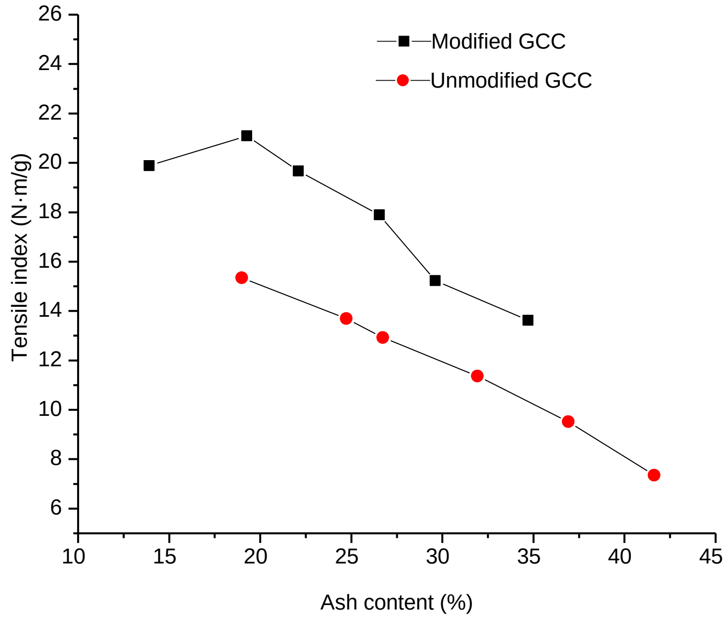

Fig. 6. Tensile index as a function of ash content in paper containing different size GCC

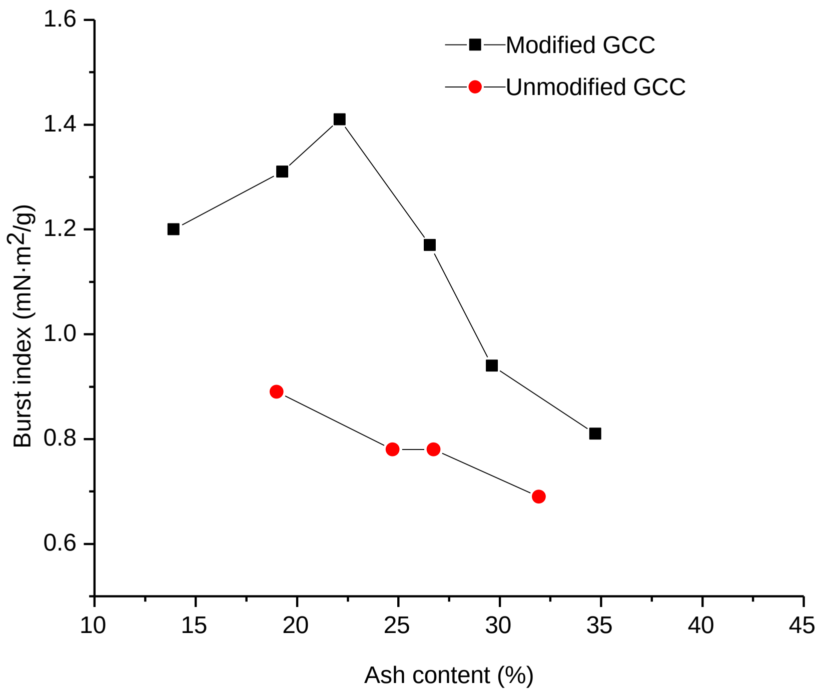

Fig. 7. Burst index as a function of ash content in paper containing different size GCC

From Fig. 7, it is clear that the burst index of paper with unmodified GCC was reduced with an increase in ash content. When the amount of filler was more than 50% (based on M_{GCC}), the burst index could not be detected. However, the burst index of paper with modified GCC was increased in the initial stage and then reduced with an increase in ash content. At the same ash content, the burst index of paper with modified GCC was higher than the unmodified GCC. When the ash content was about 23%, the burst index of paper with modified GCC was at least 70% higher than that of paper with unmodified GCC. Moreover, under comparable conditions, the burst index of paper with modified GCC was at least 30% higher than that of paper with unmodified GCC. It can be found that when the ash content was about 29.7%, the tensile index of paper with modified GCC (0.94 mN • m^2/g) was slightly higher than that of paper with unmodified GCC (0.89 mN • m^2/g) when the ash content was about 19.0%. This illustrated that the starch coated GCC had a role in increasing the paper ash content.

As shown in Fig. 8, the tear strength of paper with unmodified GCC was reduced with an increase in ash content. However, the tear strength of paper with modified GCC was increased in the initial stage and then reduced with an increase in ash content. At the same ash content, the tear index of paper with modified GCC was higher than the paper with unmodified GCC. When the ash content was about 22.10%, the tear index of paper with modified GCC was the highest at 3.61 kPa· m^2/g which was 80% higher than that of paper with unmodified GCC. Moreover, this also indicated that filler paper ash content was increased when the tear index can meet the product requirements.

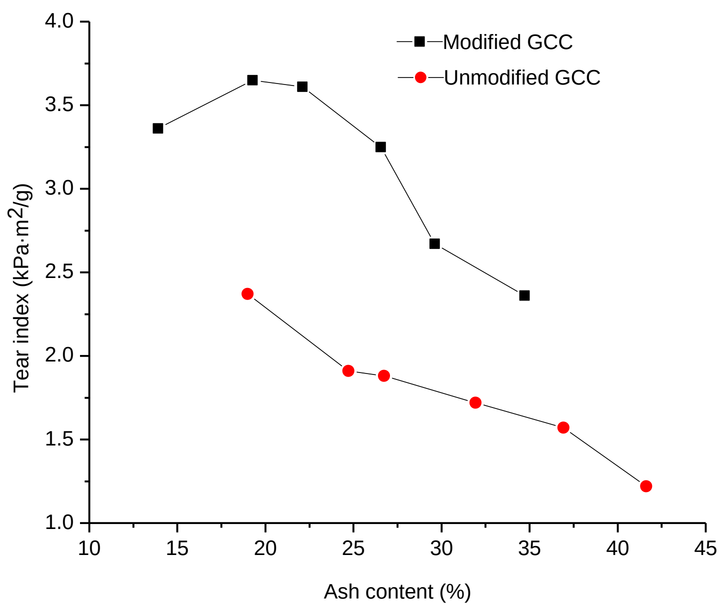

Fig. 8. Tear index as a function of ash content in paper containing different size GCC

From the above discussions, modified GCC in filler had a great influence on the physical strength of paper. As Fig. 6, 7, and 8 show, with the increase in ash content, the tensile strength, tearing strength, and bursting strength of the paper was gradually increased. This was because when starch was added in the filler, starch and plant fibers not only had the same structural units, but also they could combine with plant fibers by hydrogen bonding. When the starch was heated and dried it acted as a glue, so that the effect on filler was stronger than that of the adhesion to fiber through hydrogen bonds. This adhesion could reduce the negative impact fillers can have on paper strength properties. The strength properties of paper with modified GCC filler were much higher than those of unmodified GCC. It was believed that the strength properties of paper with modified GCC filler increased with increase in ash content.

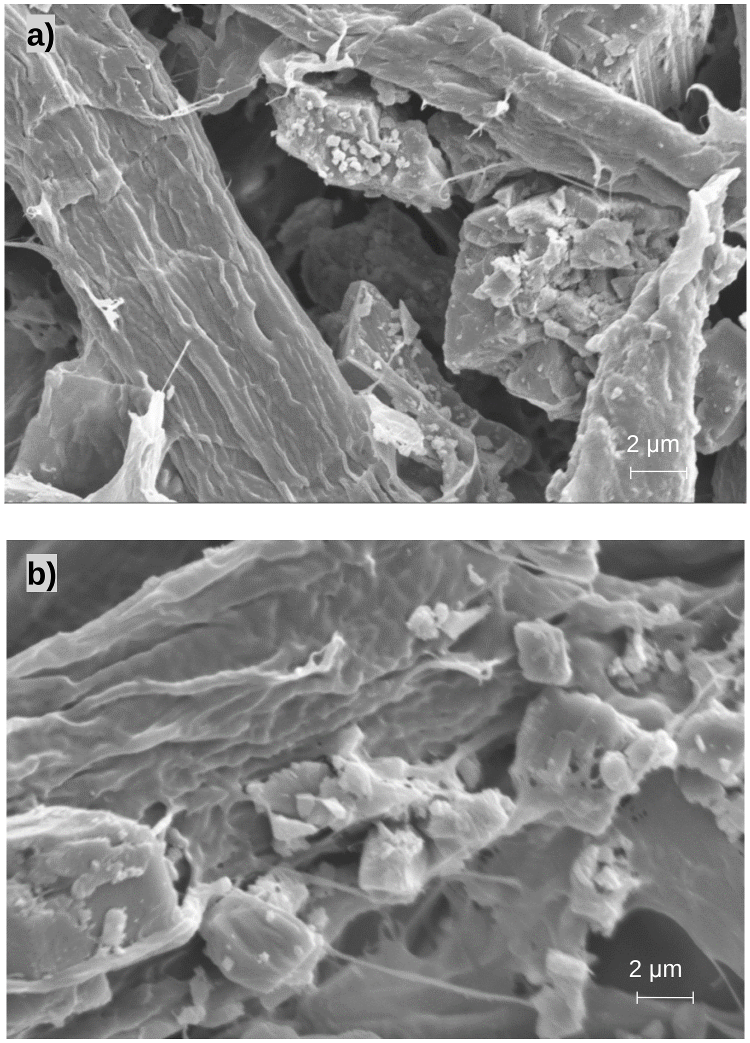

Fig. 9. SEM images of (a) unmodified GCC and (b) modified GCC

As shown in Fig. 9, the surface morphology of modified GCC was obviously different from that of the unmodified GCC. Modified GCC was coated by a layer of complex, which reduced the angular sharpness. Furthermore, the bonding between the modified GCC and the fibers was closer than that of the unmodified GCC. This occurred because the starch on the surface of the modified GCC had many hydroxyl groups, which could participate in hydrogen bonding with fibers and improve the strength properties.

Cost Considerations

The price of bleached eucalyptus pulp is 4500 to 4850 RMB / ton, the corn starch price is 2850 to 3000 RMB / ton, the heavy calcium carbonate paper price is 650 to 700 RMB / ton, the sodium stearate price is 8700 to 10000 RMB / ton, and the sodium hexametaphosphate price is 3000 to 4000 RMB / ton. The cost of a ton of modified GCC (pulp is 4,500 RMB, the rest is the maximum price): heavy calcium carbonate is 558 RMB, 478 RMB of corn starch, sodium stearate is 319 RMB, 48 RMB of hexametaphosphate, management costs (electricity, labor costs) is 80, which gives a total of 1483 RMB. Producing one ton of paper added filler, of which the tensile index was 15 N•m/g, the ash content of modified GCC is about 29% (50% filler addition), and the ash content of unmodified GCC is about 19% (35% filler addition). The paper costs of modified GCC = 4500 (pulp) * 50% + 1483 (modified GCC) * 50% = 2993 RMB; The paper costs of unmodified GCC = 4500 (pulp) * 65% + 700 (GCC) * 35% = 3170 RMB. So, using the modified GCC as a filler can save 177 RMB / ton. Then producing 100 tons of paper can save about 150,000 tons pulp, and the raw material can save about 177 million RMB. Thus, not only greatly reduce the production costs and increase corporate profits, but also for environmental protection the significance is immeasurable.

CONCLUSIONS

1. The precipitation temperature and the amount of the crosslinking agent, sodium hexametaphosphate, both contributed to shear tolerance of agglomerated calcium carbonate filler. A lower the precipitation temperature was beneficial for starch coating of the filler particles. Within a certain range, the greater the amount of sodium hexametaphosphate there was, the stronger was the shear tolerance of the complex.
2. The precipitation temperature and the amount of hexametaphosphate both affected the particle size of modified GCC. The curve decreased first and then increased, which was related to the dispersion and flocculation of modified GCC.
3. The particle size distribution curve of modified GCC was unimodal, but a second peak appeared in the 100 to 1000 μm region due to shearing.
4. At the same ash content, the negative impact on paper strength properties (tensile index, burst index, and tear index) of modified GCC filler was less than that of unmodified GCC filler. Meanwhile, after the fillers were modified with starch, the whiteness, opacity, particle size and distribution of fillers were improved.

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