Effect of Silica Gel in Causticized Calcium Carbonate from Nonwood Pulping on the AKD Sizing Efficiency of Paper

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The application of causticized calcium carbonate (CCC) from nonwood pulping as a filler in papermaking is restricted by a marked decrease in alkyl ketene dimer (AKD) sizing efficiency. But the reason for this adverse effect has not been clear. In this paper, effect of carbonization on the AKD sizing efficiency was investigated systematically. The results showed that the hydrated calcium silicate (C-S-H) in the original CCC had been converted into silica gel after carbonization, and this caused the carbonized CCC to have a higher specific surface area and larger pore volume. This could explain the reason why the CCC had a worse AKD sizing efficiency than the conventional $CaCO_3$ fillers. In addition, the effect of pH value of carbonization on the AKD sizing efficiency was also studied. It was discovered that the silica gel generated and the AKD sizing efficiency started to decline dramatically at the pH value of 8.5. Based on the research above, it can be included that pH value of 8.5 is an appropriate pH of carbonization end to maintain the AKD sizing efficiency at a good level.

Keywords: AKD sizing efficiency; Carbonization; Causticized calcium carbonate; Filler; Solid waste; Silica gel

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INTRODUCTION

Currently, with increasing environmental problems, the recycling and reutilization of solid wastes has become more prevalent, aligning well with the strategy of “sustainable development” (Zhang *et al.* 2014). Causticized calcium carbonate (CCC), a by-product produced in the alkali recovery process of the papermaking industry, is usually sent to the landfill or piled as a solid waste in the past (Tang 2003). This has not only brought serious environmental pollution, but also caused a great waste of resources. In recent years, much effort has been made by scholars to explore the recycling strategy of CCC. Currently, most of the CCC produced from wood fiber pulping has been reused by calcining to regenerate quicklime, but the CCC produced from nonwood fiber pulping (nonwood CCC) cannot be reused in this way due to a silicon problem (Pekarovic *et al*. 2006; Pan *et al*. 2009).

At present, the most extensive method to reuse nonwood CCC is to be a substitute for $CaCO_3$ fillers in papermaking. To meet the requirements for use as fillers, the CCC obtained from the causticizing process usually needs to be purified by washing, grinding, and carbonizing. However, it has been observed that the efficiency of sizing with alkyl ketene dimer (AKD) is obviously decreased when using nonwood CCC as a paper filler, *i.e.*, more AKD will be needed during the same filler loading conditions (Hu *et al*. 2011;

Liu *et al*. 2014). So far, the reason for this adverse effect is not very clear. Many researchers believe that the reason is that CCC has a higher specific surface area and larger pore volume compared with the commercial $CaCO_3$ fillers, such as ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC). These CCC fillers will adsorb more AKD particles in the wet end of papermaking. As a consequence, more AKD would be adsorbed on the fillers rather than to the cellulose fibers, thus resulting in a low sizing efficiency (Wang *et al*. 2014; Yang *et al*. 2016; Wang *et al*. 2017). However, the reason why nonwood CCC has a higher specific surface area and larger pore volume is still unknown.

A previous study by the co-authors' team has found that the acid insoluble matter in calcium carbonate from straw pulping is the main factor affecting the efficiency of AKD sizing. It was presumed that this effect may be caused by the conversion of hydrated calcium silicate (C-S-H) to silica gel in the process of carbonization (Su *et al*. 2013). But there has been no valid proof to confirm it. In this study, the differences between original CCC and carbonized CCC, including physical properties, chemical components, and sizing performance, were investigated systematically. The reason why nonwood CCC had a bad sizing efficiency was explained scientifically. Meanwhile, a potential solution for improving the AKD sizing efficiency on nonwood CCC filled paper is proposed.

EXPERIMENTAL

Materials

Original CCC (washed after obtaining from causticizing process), carbonized CCC and PCC were both obtained from a paper mill in China. The valuable information of these two samples is listed in Table 1. The AKD emulsion (with a solid content of 16.68%), cationic polyacrylamide (CPAM; with a molecular weight of 8,000,000), and hardwood bleached kraft pulp (HBKP) were also acquired from the same paper mill.

Table 1. The Valuable Information of Two Kinds of CCC

Type of Filler	$Ca(OH)_2$ (%)	NaOH (%)	Acid Insoluble Matter (%)	pH Value
Original CCC	4.65	1.07	8.35	11.69
Carbonized CCC	0.53	0.32	8.65	7.76

Methods

Extraction of silica gel

A suspension of original CCC with a concentration of 10% was first prepared. Then, 1 mol/L HCl solution was dropped into the suspension until the CCC was completely dissolved. Next, the suspension was filtered and washed with deionized water until the filtrate did not produce white sediments when tested with 1 mol/L $AgNO_3$ solution. A part of the filter residue was oven-dried at 105 °C for 4 h, and the other part was diluted with deionized water to form a suspension with a solid content of 10% for further loading use.

Carbonization of original CCC

A suspension of original CCC with a concentration of 10% was prepared and stirred at a room temperature. Carbon dioxide was then blown into the suspension to start the carbonization reaction until the pH value of the suspension reached the target value and stabilized for more than 4 h. According to the different predetermined target pH values (7.5, 8, 8.5, 9.5, 10.5, and 11.5), six kinds of carbonized CCC with different carbonization degrees were obtained.

Preparation of handsheets

The HBKP was beaten to 43 °SR and diluted to a suspension of 0.5%. Then 0.35% AKD, 0.04% CPAM, and 25% fillers (all based on the oven-dry stock) were added into the suspension and mixed by stirring. The mixture was poured into the Rapid-Koethen sheet former to prepare handsheets with a basis weight of 60 g/m^2. The wet handsheets were pressed under a pressure of 4 kg/cm^2 for 3 min and dried at 95 ℃ for 5 min.

Determination of AKD sizing efficiency

The Cobb$_{60}$ value is usually used to evaluate AKD sizing efficiency. It is defined as the absorbed amount of water on an area of 1 dm^2 when one side of the papersheet is exposed to a water pressure of 1 cm height for 60 s at the temperature of 23 °C ± 1 °C. The obtained handsheets were conditioned at 23 °C ± 1 °C and at a relative humidity of 50% ± 2% for 24 h before their Cobb$_{60}$ values were calculated according to Eq. 1,

$$\text{Cobb}_{60} = (m_a - m_b) \times 100 \qquad (1)$$

where m_a is the weight of the sheet exposed to water (g), and m_b is the weight of the sheet before exposure (g).

Analysis of Fourier transform infrared (FT-IR) spectra

The FT-IR spectra of CCC and silica gel were obtained *via* a FT-IR spectrometer (Bruker Company, Karlsruhe, Germany). Each spectrum comprised of an average of 32 scans, recorded with OPUS software (Bruker Company, version 6.1, Karlsruhe, Germany) in the wavenumber range of 400 cm^{-1} to 4000 cm^{-1} with a resolution of 2 cm^{-1} using a potassium bromide (KBr) disc. The KBr was pre-dried in the laboratory oven to reduce the interference from water.

Determination of physical properties of CCC

The detection of particle size was conducted using a 2000MU Malvern particle size analyzer (Malvern Company, Malvern, England). The specific surface area and total pore volume were measured by surface area measurement (Quantachrome NOVA 2000e, Orlando, America).

Observation of micromorphology

The surface morphology of CCC and silica gel was observed using a scanning electronic microscope (SEM; Hitachi S-3400, Tokyo, Japan) at a typical accelerating voltage of 15 kV. The samples were sputter-coated with gold (Hitachi, Tokyo, Japan) for 240 s by a S150 sputter coater prior to the SEM observation.

RESULTS AND DISCUSSION

Effect of Carbonization of CCC on AKD Sizing Efficiency

To study the effect of carbonization of CCC on AKD sizing efficiency, the original CCC, ground CCC, and carbonized CCC were used as fillers to prepare handsheets. The average particle size of CCC samples and the $Cobb_{60}$ value of the obtained handsheets are shown in Fig. 1. As shown, the average particle size of original CCC and ground CCC was very different, but their $Cobb_{60}$ value was almost the same, which indicated that the particle size of CCC had little influence on the AKD sizing efficiency. The handsheet filled with carbonized CCC had a very high $Cobb_{60}$ value that reflected its low sizing efficiency, which proved that the carbonization of CCC probably had a negative impact on the sizing efficiency.

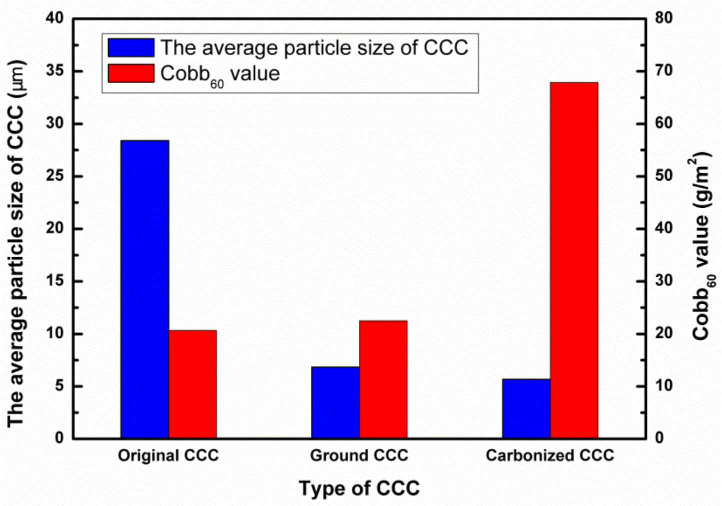

Fig. 1. The average particle size and *Cobb*$_{60}$ value of original, ground, and carbonized CCC

Demonstration of the Generation of Silica Gel During Carbonization and Its Effect on AKD Sizing Efficiency

The nonwood CCC generally contains a certain amount of acid insoluble matter, in which the main component is the silicon matter. The acid insoluble matter of the CCC used in this study was approximately 8.35% (based on the dry weight of the filler), as listed in Table 1. The authors' previous study conjectured that the hydrated calcium silicate (C-S-H) might transform into silica gel in the carbonization (Su *et al*. 2013). To confirm this hypothesis, the chemical structure, physical properties, and micromorphology of original CCC, carbonized CCC, and silica gel extracted from original CCC were studied and compared.

The FT-IR spectra of original CCC, carbonized CCC, and silica gel are shown in Fig. 2. The peak at 3690 cm^{-1} in original CCC is the characteristic adsorption peak of -OH in calcium hydroxide (Guo *et al*. 1984). The absorption peak at 970 cm^{-1} is assigned to the stretching vibration of Si-O in C-S-H, which also confirmed the existence of C-S-H in the original CCC (Yu *et al*. 1999; García-Lodeiro *et al*. 2008). The characteristic absorption peak of silica gel at 1080 cm^{-1} was observed in the silica gel sample that was extracted from the original CCC with hydrochloric acid. For the silica gel extracted from

CCC with hydrochloric acid, the strong and wide absorption band at 1080 cm^{-1} is assigned to the antisymmetric stretching vibration of Si-O-Si (Hidalgo *et al*. 2008; Wu and Ye 2016). This absorption was also observed in the carbonized CCC, indicating that C-S-H had been converted into silica gel after the carbonization. In addition, the peak at 3690 cm^{-1} was not present in carbonized CCC, which confirmed that nearly all of the calcium hydroxide had been carbonized into calcium carbonate, which was consistent with the results showed in Table 1. Therefore, it is possible to speculate that the following reaction will occur in CCC during the carbonization:

$$\text{C-S-H} + CO_2 \rightarrow CaCO_3 + SiO_2 \cdot nH_2O \qquad (1)$$

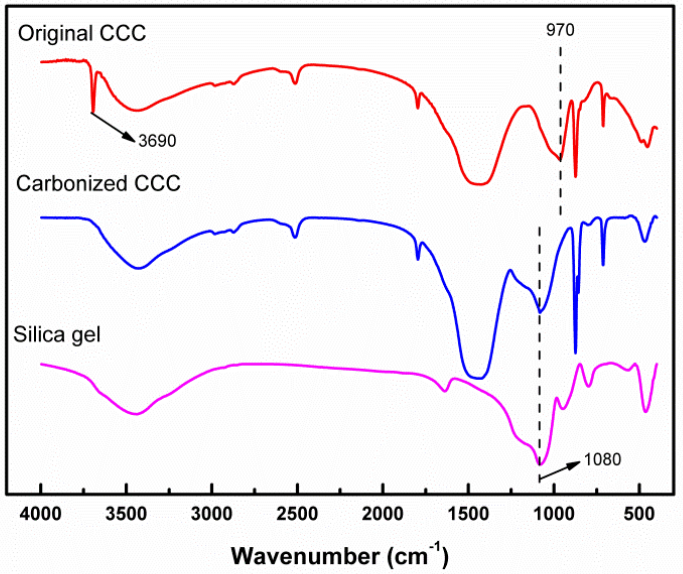

Fig. 2. The FT-IR spectra of original CCC, carbonized CCC, and silica gel

The specific surface area, total pore volume, and Cobb$_{60}$ value of original CCC, carbonized CCC, and silica gel are listed in Table 2. The specific surface area and total pore volume of CCC increased remarkably after carbonization. The Cobb$_{60}$ value of carbonized CCC was approximately four times higher than that of original CCC, confirming that the sizing efficiency was greatly reduced after the carbonization. The main reason for this decline was likely due to the increase in the specific surface area of CCC. It has been found that the silicon content of CCC is proportional to its specific surface area (Xia *et al*. 2015). Combined with the FT-IR analysis and the quite high specific surface area and Cobb$_{60}$ value of silica gel, it can be inferred that the increase of the specific surface area and pore volume of CCC was due to the formation of silica gel during the carbonization.

Table 2. Physical Properties of Original CCC, Carbonized CCC, and Silica Gel

	Original CCC	Carbonized CCC	Silica Gel
Specific Surface Area (m^2·g^{-1})	11.973	47.784	347.855
Total Pore Volume (cm^3·g^{-1})	0.0601	0.0850	0.6699
Cobb$_{60}$ Value (g·m^{-2})	22.5	67.9	127.9

The SEM images of original CCC, carbonized CCC, and silica gel are shown in Fig. 3. It can be seen that the original CCC had a compact lump structure (Fig. 3a), while silica gel had a loose flaky structure (Fig. 3c), each of which corresponded to their specific surface area and total pore volume. The structure of carbonized CCC (Fig. 3b) was similar to that of silica gel, which indicated that the formation of silica gel was likely to be the reason for the increase of specific surface area and total pore volume of CCC after carbonization. In the sizing, AKD particles can be adsorbed on the surface of carbonized CCC by physical or electrostatic interaction according to the migration mechanism (Wang *et al*. 2017). A larger specific surface area of carbonized CCC resulted in more AKD particles that were adsorbed. After drying, the adsorbed AKD particles were filled in or coating the surfaces of the pores of carbonized CCC instead of deposited on the pulp fibers, which resulted in a remarkable decrease in the AKD sizing efficiency.

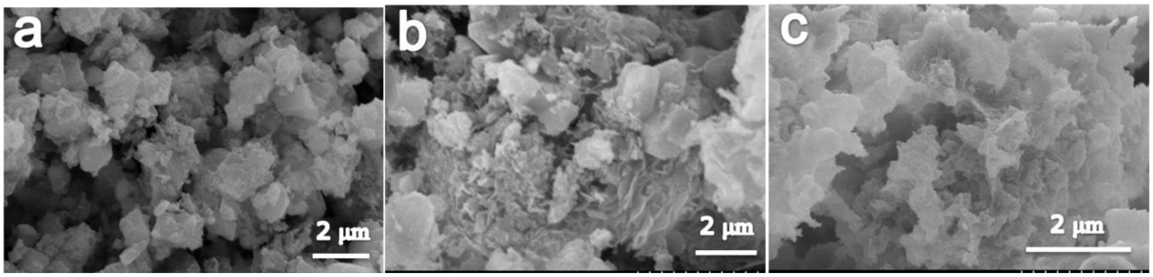

Fig. 3. Microscope images of CCC and silica gel: a: original CCC; b: carbonized CCC; and c: silica gel

Control of the Formation of Silica Gel During Carbonization

In the carbonization stage, carbon dioxide was used to reduce the pH value of the suspension to convert the excessive calcium hydroxide into calcium carbonate and neutralize the residual base. It is known that excessive residual base will affect the stability of the wet end of the paper machine, so the carbonization is very important and necessary. In fact, there was no exact pH value of carbonization end for the carbonization in practice. Generally, it is carbonized for several hours using carbon dioxide to ensure that the residual base reacts completely (Li 2002).

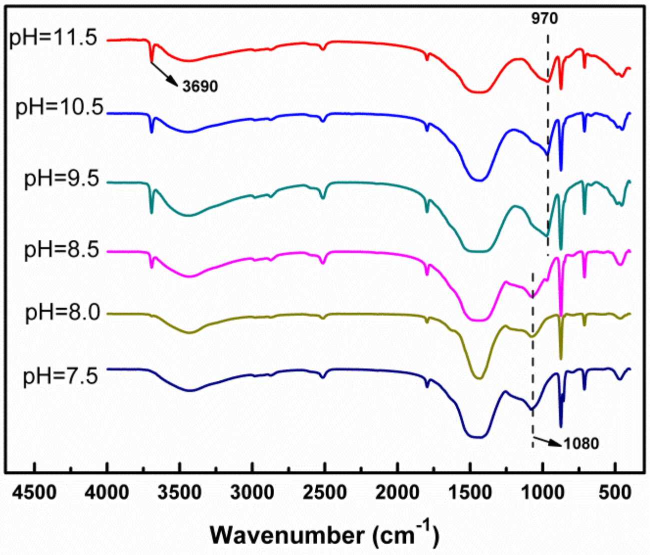

Fig. 4. FT-IR spectra of carbonized CCC samples obtained at different pH value

To study the generation of silica gel, the products obtained at different pH values after carbonization were analyzed. The FT-IR spectra of the obtained carbonized CCC are shown in Fig. 4. When the pH value of the carbonization was equal to or greater than 9.5, the obtained product had an obvious absorption peak at 970 cm^{-1}, which indicated that the silicon element existed in the form of calcium silicate hydrated. When the pH value was reduced to 8.5 or less, the absorption peak at 970 cm^{-1} nearly disappeared, and it shifted to the 1080 cm^{-1}, which indicated that the calcium silicate hydrated was gradually converting into silica gel. In addition, the absorption peak at 3690 cm^{-1} gradually weakened and disappeared, which suggested that the calcium hydroxide in the samples was gradually carbonized into calcium carbonate.

The Cobb$_{60}$ values of the handsheets filled with the obtained carbonized CCC samples at different pH values are shown in Fig. 5. It can be seen that the Cobb$_{60}$ value of the handsheets increased gradually from 22.3 g/m^2 to 34.1 g/m^2 when the pH value of carbonization reduced from 11.5 to 8.5, while the Cobb$_{60}$ value increased sharply from 34.1 g/m^2 to 67.9 g/m^2 when the pH value was reduced from 8.5 to 7.5. This was also consistent with the research above, namely that the formation of silica gel in CCC greatly reduced the sizing efficiency of AKD. Furthermore, the AKD sizing efficiency of paper filled with nonwood CCC can be improved by controlling the pH value of the carbonization. Moreover, the main purpose of carbonization is to remove the residual alkali, especially calcium hydroxide, in the original CCC to ensure the stability of the wet end of paper machine. It was concluded that the optimum pH value for carbonization could be set to 8.5, which can improve the AKD sizing efficiency and ensure the removal of most of the calcium hydroxide. Therefore, controlling the pH value of carbonization could be an effective way to solve the difficult use of nonwood CCC for papermaking fillers because of their high silicon content, and could thus help to promote the recovery and utilization of nonwood CCC in the paper industry.

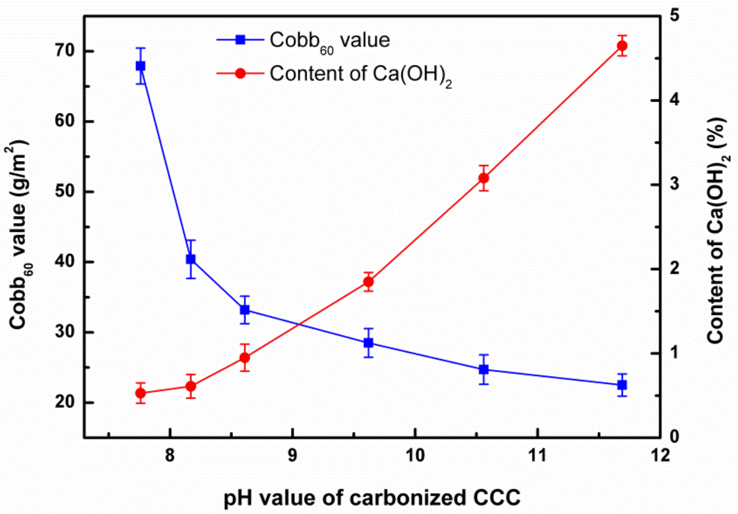

Fig. 5. The changes of *Cobb*$_{60}$ value and content of calcium hydroxide with the carbonization

The pH at the end of carbonization was controlled to a value of 8.5, and then a comparison was made with PCC under the same loading conditions. The results are shown in Table 3. It could be found that the Cobb$_{60}$ value had a remarkable decrease after optimization (controlling the pH value of carbonization), from 67.9 g/m^2 to 34.1 g/m^2. But compared with the PCC, it still showed a difference. Our further study will focus on other methods to improve the CCC's sizing efficiency, aiming to expand the application of CCC as a low-cost filler for the paper industry.

Table 3. Sizing Difference of PCC and Two Kinds of CCC

Type of Filler	PCC	CCC before Optimization	CCC after Optimization
Cobb$_{60}$ Value ($g \cdot m^{-2}$)	19.6	67.9	34.1

CONCLUSIONS

1. In this paper, the effect of CCC from nonwood pulping on the AKD sizing efficiency of filled paper was studied. The results showed that the carbonization of CCC had a much greater influence on the AKD sizing efficiency compared with the grinding process. The analysis of chemical structure and micromorphology of CCC and extracted silica gel showed that the hydrated calcium silicate in CCC was changed into silica gel during the carbonization. The generation of silica gel increased the specific surface area of CCC four fold.
2. By controlling the pH value of the carbonization, the generation of silica gel was reduced. The optimal pH value was 8.5, at which most of the calcium hydroxide in CCC was transformed into calcium carbonate, and the AKD sizing efficiency of filled paper was improved remarkably.

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