AKD Sizing Efficiency of Paper Filled with $CaCO_3$ from the Kraft Causticizing Process

Jian Wang,[a,b,]* Ling Liu,[a] Zhijie Wang, [a] and Yongjian Xu [a]

Causticizing calcium carbonate (CCC), known as lime mud, is a by-product of the papermaking industry that comes from the green liquor causticizing process. In China, CCC has been used as a paper filler to replace precipitated calcium carbonate (PCC). This is beneficial for saving resources and preventing secondary pollution. Unfortunately, compared with PCC, CCC can reduce the sizing efficiency of alkyl ketene dimer (AKD). So the application scope and dosage of CCC has been limited in mill trials in China. In this study, CCC was prepared with green liquor and quicklime, which were obtained from an alkali recovery line of a pulping mill. The reason for the lower sizing efficiency of AKD when CCC was used as a filler was investigated. The results showed that when greater amounts of AKD were adsorbed by CCC, the AKD sizing efficiency was lower. The irregular CCC had higher Brunauer, Emmett, and Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) method cumulative desorption pore volume, resulting in higher adsorption. The spindle-like or needle-like CCC had lower BET surface area and BJH method cumulative desorption pore volume that was beneficial for controlling its adsorption of AKD and improving the sizing efficiency.

Keywords: Causticizing calcium carbonate; Sizing efficiency; Alkyl ketene dimer; Filler; Adsorption

*Contact information: a: College of Light Industry and Energy, Shaanxi University of Science & Technology, Xi'an 710021, China; b: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510640, China; *Corresponding author: zzwangjian@sust.edu.cn*

INTRODUCTION

Environmental protection has been one of the main drivers for sustainable development of the pulp and paper industry, resulting in more paper mills focusing on effective treatment of solid waste. Causticizing calcium carbonate (CCC), known as "lime mud" or "lime sludge," is a by-product that comes from converting green liquor to white liquor during the alkali recovery process. For wood materials, CCC can be calcined in a rotary lime kiln after being dewatered and recirculated in the causticizing process. For non-wood materials, however, this is not practical due to a serious silica problem (Pekarovic *et al*. 2006). There have been many efforts to solve this problem, for example, by adding Al_2O_3, CaO, and MgO during the cooking process (Tutus and Eroglu 2004), but further studies must be carried out to reduce the content of silica. In China, CCC from non-wood materials is usually discarded as solid waste or used in landfill after dewatering. Secondary pollution occurs because of a small amount of $Ca(OH)_2$ in the CCC (Tang and Liu 2003). CCC, as a kind of $CaCO_3$, can be used as paper filler, which can in turn prevent secondary pollution. Furthermore, CCC costs 30 to 50 USD/ton less than commercial precipitated calcium carbonate (PCC) (Wang and Yang 2011). If the properties of CCC are suitable for use as paper filler, then the paper industry could reap remarkable social and economic benefits (Konnoa *et al*. 2009; Li and Wang 2007).

In China, several CCC filler producing lines have been completed, and the CCC has been used as filler for paper. From mill trials (Pan *et al*. 2009; Wang 2008), it was determined that some amount of PCC can be replaced with CCC. Unfortunately, when the CCC is used as filler, there is lower sizing efficiency of AKD compared to that of PCC. So the application scope and dosage of CCC have been limited. The sizing efficiency of AKD affected by the filler, such as PCC or ground calcium carbonate (GCC), had been studied (Karademir *et al*. 2005; Lindström and Larsson 2008; Lindström and Glad-Nordmark 2007), but not involving the CCC. In the present study, the reason for the lower sizing efficiency of AKD was investigated in order to provide technical support for CCC quality improvement during the causticizing process of non-wood pulping alkali recovery.

EXPERIMENTAL

Materials

Green liquor from non-wood pulp (Table 1), quicklime, PCC, AKD (15% solids content, 80% active AKD content), NBKP, LBKP, and CPAM were all obtained from mills in China. Three kinds of mill CCCs were obtained from different mills in China. The properties of PCC and CCCs are shown in Table 2.

Table 1. Main Components of Green Liquor from Straw Pulp

	Na_2CO_3	NaOH	SiO_2	Insoluble matter
Content ($g \cdot L^{-1}$)	138.21	28.65	6.45	2.36

Table 2. Properties of PCC and CCCs

No.	Material	Brightness (%ISO)	Avg. particle size (μm)	Content of $CaCO_3$ (%)	pH value	Sediment volume ($mL.g^{-1}$)
1	PCC	92.80	4.03	97.56	9.73	2.8
2	CCC #1	88.36	4.38	92.33	9.32	2.4
3	CCC #2	85.22	5.15	93.43	9.90	2.3
4	CCC #3	87.35	5.03	92.50	10.23	2.6

Preparation of CCC

To prepare the CCC, quicklime was added to a flask, which was filled with water and stirred at 300 rpm to achieve slaking. Then, green liquor that was filtered by slow filter paper, was added to the flask at a constant rate with a transfusion tube, and the causticizing reaction was carried out. The molar ratio of $Ca:CO_3^{2-}$ was 1.05:1. The reaction temperature was varied from 70 °C to 90 °C, and the reaction time was 2 h. After these reactions, the CCC was filtered and washed with water, then diluted to 20% and injected with CO_2 until the pH was in the range of 9.0 to 9.5. After carbonation, the portion of CCC that passed through an 800-mesh screen was washed with water and used as a filler.

Adsorption of AKD

The experiment was designed in two steps. In the first step, using an ultraviolet spectrophotometer, the absorbance of different concentrations of AKD was determined at a wavelength of 238 nm, and the standard curve was drawn. In the second step, AKD was added into the CCC suspension in a ratio of 1:100 and stirred for 5 min. Then, the mixture was centrifuged for 10 min at 3000 rpm. The supernatant liquor was used to determine absorbance at the wavelength 238 nm. The content of AKD in the supernatant liquor was calculated according to the standard curve. The AKD adsorbed by CCC was equal to the difference between the dosage of AKD and the content of AKD in the supernatant liquor.

Determination of Physical Properties of CCC

The determination of particle size was carried out using a BT-9300H laser particle size analyzer. The determination of BET and BJH was carried out according to an Autosorb-iQ.

Sheet Forming

0.2% AKD was added to the dispersed stock after 60 s stirring, and 30% PCC or CCC was added. Then, 0.03% CPAM was added after 30 s stirring, the stock was poured into the Rapid-Koethen sheet former, and handsheets were prepared with a basis weight of 80 g/m^2. The wet paper was pressed for 3 min under 4 kg/cm^2 of pressure and dried for 5 min at 95 °C.

RESULTS AND DISCUSSION

Sizing Efficiency of AKD in Filled Paper

The sizing efficiency of AKD in CCC or PCC filled paper is shown in Table 3.

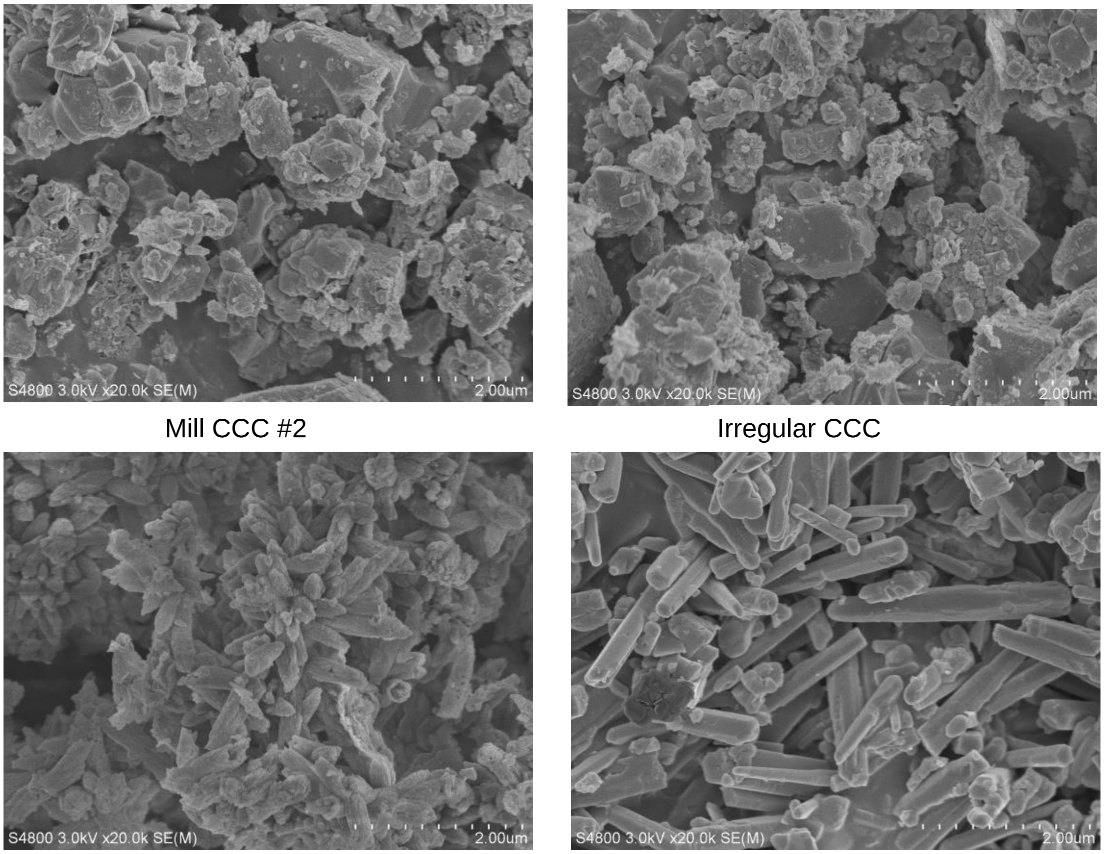
Table 3. Sizing Efficiency of AKD in Filled Paper

Type of filler	PCC	CCC #1	CCC #2	CCC #3
$Cobb_{60}$ ($g \cdot m^{-2}$)	24.3	70.2	86.1	123.4

As shown in Table 3, compared with PCC filler, the $Cobb_{60}$ values of paper filled with CCC fillers were much higher, which displayed the lower sizing efficiency of AKD. The results showed that there must be differences in the properties of CCC and PCC, which caused the lower sizing efficiency of AKD in the CCC-filled paper. The Cobb60 values of paper filled with CCC #2 was at an intermediate level. Notably, the physical properties of CCC #2 were intermediate level too. So the mill CCC #2 was used to study the effects on the sizing efficiency of AKD based on the thinking that its characteristics were neither too high nor too low.

Effect of Adsorption of AKD

According to the literature (Nanri *et al*. 2008; Wang *et al*. 2012), the irregular, spindle-like, and needle-like CCCs were obtained by precisely controlling its causticizing reaction.



Mill CCC #2 Irregular CCC

Spindle-like CCC Needle-like CCC

Fig. 1. SEM Photographs of CCCs (20000×)

When the three kinds of CCCs were used as filler, it was surprising to find that the $Cobb_{60}$ values of paper filled with spindle-like or needle-like CCCs were approximately the same as that of PCC (Table 4).

Table 4. $Cobb_{60}$ Values of Filled Paper

No.	Type of filler	$Cobb_{60}$ ($g \cdot m^{-2}$)
1	PCC	25.6
2	Mill CCC #2	84.8
3	Irregular CCC	82.2
4	Spindle-like CCC	26.5
5	Needle-like CCC	20.2

As stated in the literature (Bartz *et al*. 1994), increasing amounts of AKD adsorbed by the filler led to higher $Cobb_{60}$ values and lower AKD sizing efficiency. Therefore, the amount of AKD adsorbed by the filler was measured, and the results are shown (Table 5). Notably, more AKD was adsorbed by mill CCC #2 or irregular CCC than PCC, but approximately the same amount of AKD was adsorbed by spindle-like or needle-like CCC as on the PCC. These results provide a likely explanation as to why the $Cobb_{60}$ value of paper filled with spindle-like or needle-like CCC was approximately the same as that obtained for paper filled with PCC.

Table 5. Content of AKD Adsorbed by the Filler

No.	Type of filler	AKD adsorbed (mg/g)
1	PCC	4.382
2	Mill CCC #2	6.247
3	Irregular CCC	6.777
4	Spindle-like CCC	4.121
5	Needle-like CCC	3.870

Physical Properties of filler and Mechanism of effect on Sizing Efficiency

The physical properties of fillers were measured, and the results are shown in Table 6.

Table 6. Physical Properties of Fillers

No.	Type	Avg. Particle size (μm)	BET (m^2/g)	BJH method cumulative desorption pore volume (cm^3/g)
1	PCC	4.03	4.623	1.38E-02
2	Mill CCC #2	5.15	22.663	4.26E-02
3	Irregular CCC	5.87	12.405	4.67E-02
4	Spindle-like CCC	6.85	3.996	8.73E-03
5	Needle-like CCC	5.69	4.505	8.17E-03

Compared with PCC, the mill CCC #2 and the irregular CCC had much higher BET and BJH, but the CCC with a regular crystal, spindle-like, or needle-like structure had lower BJH and approximately the same BET surface area as the PCC. In the causticizing reaction process, there are two correlated reactions. One is the formation of the crystal nucleus, and the other is the growth of the crystal particle. When the rate of the crystal nucleus formation is lower than that of the crystal particle growth, the shape of the CCC can be controlled. During the growth of the crystal particle, a dense structure of CCC with lower pore volume is produced. When the rate of crystal nucleus formation is higher than that of crystal particle growth, crystal nuclei generate rapidly and aggregate together. Pores will emerge in the course of linking of particles into aggregations. This is the reason why the CCC with the regular crystal structure had lower BET and BJH than that of irregular CCC.

It is well known that the sizing process of AKD occurs in three consecutive steps: retention, spreading, and reaction. The sizing efficiency has been shown to be directly linked to the amount of reacted AKD. In the paper drying process, melting and spreading of the AKD wax precedes reaction with cellulose hydroxyl groups on the fiber surfaces. Greater amounts of AKD are adsorbed by mill CCC #2 or irregular CCC, which both have higher BET, as shown in Table 5. The AKD that is adsorbed by the filler will spread out as AKD molecules and migrate into the void structure of the CCC pores during the drying process. When the AKD retained on the surface of fiber is spreading, a portion of the AKD molecules in contact with the surface of CCC can also migrate into the void structure. These AKD molecules are then unavailable for sizing. The higher cumulative desorption pore volume, based on the BJH method, means that there will be more capacity to accommodate AKD. It was hypothesized that CCC with a smaller specific pore volume can lead to a higher fraction of available AKD. Therefore, when the BJH pore volume is higher, the sizing efficiency is lower. This hypothesis provides an explanation as to why there is lowered sizing efficiency when conventional CCC is used to fill paper. The key point to quality improvement of CCC is controlling the reaction conditions of the causticizing process and producing CCC with a regular crystal structure.

CONCLUSIONS

1. For paper filled with causticizing calcium carbonate (CCC), the greater the amount of alkyl ketene dimer (AKD) adsorbed by CCC, the lower will be the sizing efficiency of AKD.
2. In comparison with a commercial PCC filler product, irregular CCC had higher BET and BJH method cumulative desorption pore volume, resulting in higher adsorption capacity for AKD. The spindle-like or needle-like CCC had lower BET surface area and BJH method cumulative desorption pore volume, which was beneficial for controlling its adsorption of AKD and improving the sizing efficiency.

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