Hydrophobicity of Lime Sludge Filled Paper Assisted by a Cationic Starch/CPAM/Bentonite Retention Aids System

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Lime sludge is a special type of precipitated calcium carbonate (PCC) recovered from black liquor, which can be used as paper filler in the paper-making process. However, one of the biggest problems when lime sludge is used as filler is that it is difficult to hydrophobically size the filled paper, especially in the case of paper with high filler content. Also, the efficient retention of the sizing agent AKD is a fundamental requirement for effective paper hydrophobic sizing. Therefore, in this work, a ternary retention aids system, cationic starch/CPAM/bentonite, was applied, and the hydrophobic sizing degree of lime sludge filled paper sheets and filler retention were evaluated. The results showed that the retention of lime sludge was significantly influenced by CPAM and was overall increased as the dosage of CPAM increased; cationic starch showed a more significant influence on paper Cobb value than filler retention; relative lower Cobb values and higher filler retention were achieved at lower bentonite dosage. At 0.75% cationic starch, 0.043% CPAM, and 0.3% bentonite, a substantial high hydrophobic sizing efficiency of Cobb value (45.72 g/m^2) and filler retention (80.37%) were achieved simultaneously due to the synergetic performance of a cationic starch/CPAM/bentonite retention aids system.

Key words: Filler retention; AKD sizing; Lime sludge; Cationic starch; CPAM; Bentonite; Retention aids system

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INTRODUCTION

Lime sludge is a by-product of recovering alkali from the non-wood pulping process. The usual treatment, in which the sludge ends up in landfills, not only causes environmental pollution, but also leads to a waste of resources. A promising approach to avoid this wastage is to use the sludge as a paper filler in the circulation of a paper-making process. However, one of the biggest problems when lime sludge is used as filler is that it is difficult to achieve hydrophobic sizing.

The term "hydrophobic sizing" used in papermaking is the process by which a chemical additive provides paper and paperboard with resistance to liquid wetting, penetration, and absorption. Cellulose is hydrophilic with a high surface energy. The porous structure of paper acts like a sponge in the presence of liquid. The purpose of hydrophobic sizing agents is to reduce the surface energy of cellulose so that it can have some protection against liquid absorption (Hagemeyer *et al.* 1992). In the modern alkaline papermaking industry, the most common alkaline hydrophobic sizing agents are alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA). Both ASA and AKD have been shown to be effective and have been used as internal hydrophobic sizing agents in papermaking for many years (Hodgson *et al.* 1994; Shen *et al.* 2001; Truong *et al.* 2003; Hubbe 2007; Sharma *et al.* 2010).

AKD hydrophobic sizing is believed (Roberts 1989; Lindstrom and Eklund 1991) to occur by a three-step mechanism involving (1) the retention of AKD particles (0.5 to 1 μm) on the pulp fibers; (2) the spreading of AKD particles to a monolayer thickness film; and (3) some re-conformation, probably involving the establishment of a covalent cellulose–AKD bond. AKD can react with the hydroxyl groups of cellulose to form a β-keto-ester, or with water to form a β-keto-acid. Whatever the principle is, the first step is essentially important for AKD sizing. Furthermore, once AKD hydrolyses, the efficiency of AKD sizing will decrease.

As is well known, using calcium carbonate as filler will cause a decline in paper sizing degree. And as the amount of calcium carbonate filler increases, the sizing degree of paper will decrease accordingly, especially in paper filled with lime sludge (He *et al.* 2014; Wang *et al.* 2014). Therefore, when the filler is lime sludge, the retention of AKD is far more important.

So in order to obtain a better sizing effect with less AKD agent, more research on the retention of AKD sizing agents should be done. In this paper, we mainly discuss the effect of a ternary retention system (cationic starch/cationic polyacrylamide (CPAM)/ bentonite) on AKD sizing efficiency and filler retention. The influence of the combination of cationic starch, CPAM, and bentonite on the sizing effect of AKD was investigated, and the related mechanism is discussed.

EXPERIMENTAL

Materials

Lime sludge, precipitated calcium carbonate (PCC), chemi-thermo-mechanical pulp, reed pulp (amur silver grass pulp), bleached sulfate softwood pulp, cationic starch (CS), AKD dispersion (solid content of 17.5%), cationic polyacrylamide (CPAM) (molecular weight of 8 million grams per mole, charge density of 2.47 mmol/g), and bentonite were all supplied by Yueyang paper mill (Hunan, China). The furnish was composed of 50% of chemi-thermo-mechanical pulp, 30% of reed pulp, and 20% of softwood pulp.

Methods

Handsheet preparation and testing

The order of paper preparation was: pulp → cationic starch → AKD→ CPAM → lime sludge/PCC→ bentonite → sheet formation. The pH of the stock was around 8.0, as measured by a Sartorius PB-10 acidometer (Germany). The consistency of the stock was 1% (w/v), and the time interval between AKD and fillers addition was 2.5 min. Before manufacturing paper, pulp and chemicals were mixed well by an agitator (IKA Eurostar).

Handsheets of 70 g/m^2 were formed in a RK3-KWTjul Rapid-Koethen sheet former (Australia). The filler retention ratio was determined at 575 ^oC in the Muffle furnace (Germany) (Shen *et al.* 2008), which was calculated according to the following formula,

$$Filler\ retention\ ratio(\%) = \frac{A}{m \times (1-a)} \times 100 \qquad (1)$$

where A is the ash left in paper (g), m is the weight that added in paper (g), and a is the loss mass fraction. The hydrophobicity of paper is expressed by Cobb60.

Table 1. Dosage of Ternary Retention Aids

Group	CS dosage (%)	CPAM dosage (%)	Bentonite dosage (%)	Group	CS dosage (%)	CPAM dosage (%)	Bentonite dosage (%)
1	0.5	0.018	0.2	33	0.5	0.018	0.4
2	0.75			34	0.75		
3	1.0			35	1.0		
4	1.25			36	1.25		
5	0.5	0.043		37	0.5	0.043	
6	0.75			38	0.75		
7	1.0			39	1.0		
8	1.25			40	1.25		
9	0.5	0.068		41	0.5	0.068	
10	0.75			42	0.75		
11	1.0			43	1.0		
12	1.25			44	1.25		
13	0.5	0.093		45	0.5	0.093	
14	0.75			46	0.75		
15	1.0			47	1.0		
16	1.25			48	1.25		
17	0.5	0.018	0.3	49	0.5	0.018	0.5
18	0.75			50	0.75		
19	1.0			51	1.0		
20	1.25			52	1.25		
21	0.5	0.043		53	0.5	0.043	
22	0.75			54	0.75		
23	1.0			55	1.0		
24	1.25			56	1.25		
25	0.5	0.068		57	0.5	0.068	
26	0.75			58	0.75		
27	1.0			59	1.0		
28	1.25			60	1.25		
29	0.5	0.093		61	0.5	0.093	
30	0.75			62	0.75		
31	1.0			63	1.0		
32	1.25			64	1.25		

The Cobb60 sizing value of the handsheets was measured using a ZZ-100 Cobb sizing tester (China) according to TAPPI test method T 441 om98.

Effect of lime sludge on sizing efficiency

To investigate the influence of lime sludge on AKD sizing, the Cobb value of PCC filled paper was compared. And the influence of the AKD dosage on paper filled with lime sludge and PCC was also investigated.

The combination of the three retention aids

Sixty four groups of the ternary retention aids system, cationic starch/CPAM/bentonite were applied in this experiment. In these 64 groups of tests, the dosage of AKD dispersion was 0.25% (to the amount of dry pulp), and the dosage of lime sludge/PCC was 24% (to the amount of dry pulp). In order to guarantee the total retention, cationic starch and CPAM were added in the system before and after AKD respectively to ensure that AKD had retained on the fibres and fundamentally improved the sizing effect. The dosages of the ternary retention aids are shown in Table 1.

RESULTS AND DISCUSSION

Influence of Lime Sludge and PCC on AKD Sizing

For the sizing of paper, the lower the Cobb value, the greater is the hydrophobic sizing degree. As shown in Fig. 1, the hydrophobic sizing efficiency of both lime sludge and PCC filled paper decreased sharply as the filler loading was increased. Furthermore, in the filling range of 19% to 39%, the sizing degree of lime sludge filled paper was much lower than that of PCC-filled paper, which indicated the negative influence of lime sludge. At a certain AKD content, the sizing degree of paper filled with 19% lime sludge and the hydrophobic sizing degree of paper filled with 39% PCC were almost the same. So to obtain a similar hydrophobic sizing degree, the lime sludge dosage should be 20% less than the PCC dosage. And therefore, as the lime sludge is used as a paper filler, AKD sizing efficiency is far more of a challenge.

The influence of the AKD dosage on hydrophobic sizing of paper filled with lime sludge and PCC is shown in Fig. 2. It can be found that the hydrophobic sizing effect became better with the increasing of AKD dosage for both types of filled paper. To obtain the same hydrophobic sizing degree, the AKD dosage in lime sludge filled paper was twice as much as that in the PCC-filled paper.

It is generally accepted that AKD sizing agent is consumed in filled paper due to the higher specific surface area of filler compared to pulp fiber, and filler particles are much too small to be directly retained by the typical forming fabrics (Hubbe *et al.* 2009), which resulted in the loss of AKD. The difference between the influence of lime sludge and PCC on AKD sizing may come from the morphological characteristics of lime sludge and PCC. According to our previous studies, we found that: lime sludge has wider particle size distribution, higher specific surface area, and generally larger pore sizes than commercial PCC and GCC (Table 2). It is found that the hydrophobic sizing degree of paper increases with the increase of PCC particle size (Bartz *et al.* 1994). Lime sludge fillers have a larger surface area that can consume the AKD sizing agent, and they themselves are not sized, as it is believed that reactive sizes do not react with fillers.

These differences mean that in a lime sludge filled paper system, the retention of AKD is far more important.

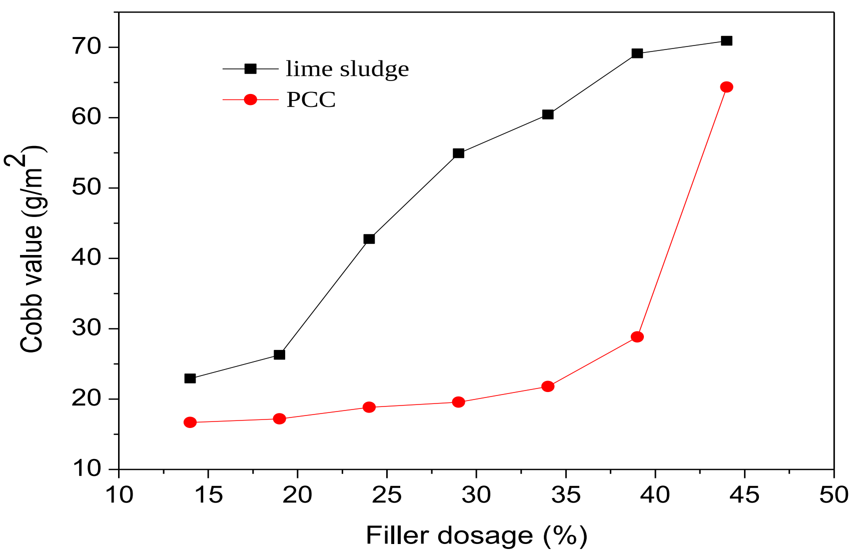

Fig. 1. The influence of dosage of lime sludge and PCC on AKD sizing (AKD dosage of 0.25%, CS dosage of 0.75%, CPAM dosage of 0.043%, bentonite dosage of 0.5%, to the amount of dry pulp)

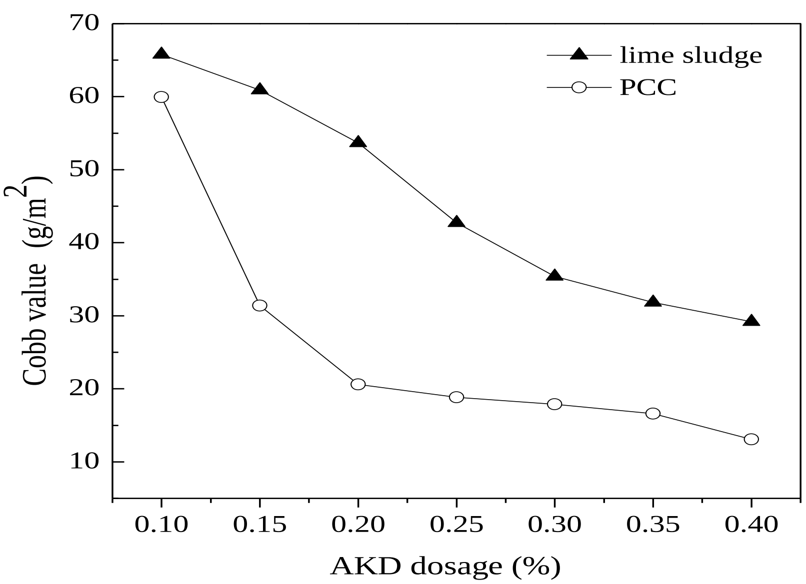

Fig. 2. The influence of the AKD dosage on paper filled with lime sludge and PCC (lime sludge and PCC dosages of 24%, CS dosage of 0.75%, CPAM dosage of 0.043%, bentonite dosage of 0.5%, to the amount of dry pulp)

Table 2. Specific Surface Area and Pore Diameter of Fillers

Kinds of fillers		BET surface area(m^2/g)	BJH average pore size (nm)	Total Pore volume (cm^3/g)
Lime sludge	1	15.0238	21.0564	0.0626
	2	13.7465	17.3015	0.0551
	3	12.2115	18.8058	0.0519
	4	10.4036	19.7334	0.0460
	5	9.8729	17.5679	0.0407
	6	9.0977	20.1335	0.0382
PCC	1	4.2346	28.5907	0.0130
	2	3.0812	32.8976	0.0137
	3	3.5481	23.0821	0.0137
	4	2.9124	27.3184	0.0129
	5	2.9736	42.9003	0.0132
	6	3.9912	23.6243	0.0165
GCC	1	6.6765	28.9250	0.0348
	2	4.2528	25.1966	0.0207
	3	4.7896	26.3284	0.0271
	4	4.4567	27.6734	0.0178
	5	3.0136	35.7104	0.0154

Influence of Retention Aids on AKD Sizing

To investigate the effect of this retention aids system on sizing efficiency of lime sludge filled paper, 64 groups of experiments involving combinations of cationic starch, CPAM, and bentonite were carried out. The results are shown in the following figures:

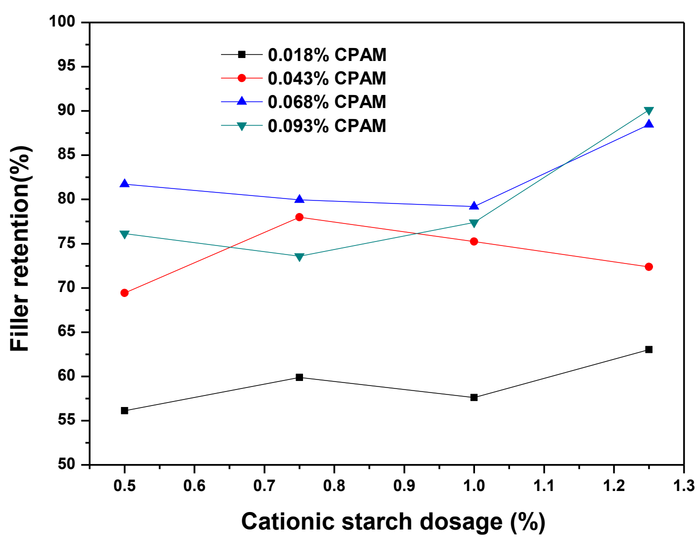

Fig. 3. The influence of the cationic starch dosage on filler retention (bentonite dosage of 0.2%)

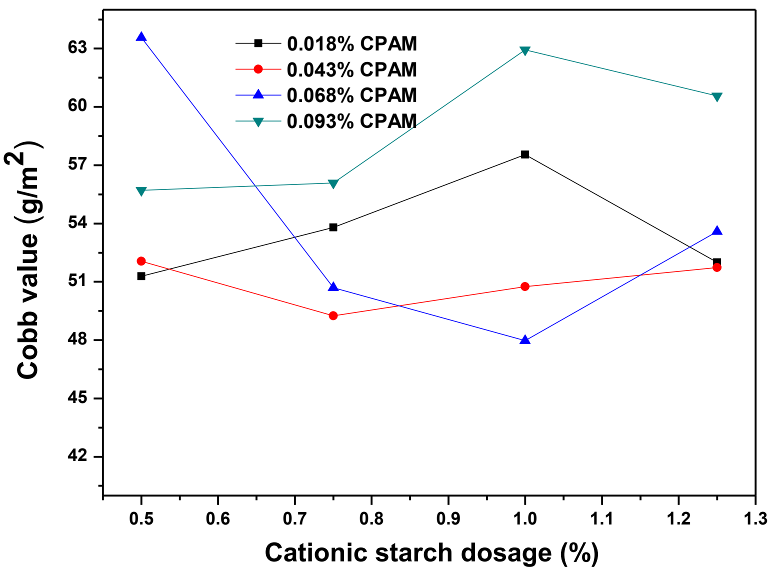

Fig. 4. The influence of the cationic starch dosage on AKD sizing (bentonite dosage of 0.2%)

Figures 3 and 4 show the filler retention and Cobb value at 0.2% bentonite. As shown in Fig. 3, the retention of lime sludge was significantly influenced by CPAM dosage. When cationic starch was less than 1%, as the dosage of CPAM was increased from 0.018% to 0.068%, the filler retention sharply increased from 56.13% to 88.47%, and then when cationic starch was equal to 1% or more than 1%, it decreased as the CPAM dosage continued to increase to 0.093%. There was a slight difference in retention at higher CPAM dosages. The reason may be that the cationic starch did not show a distinct effect on the filler retention until its dosage was more than 1%, and the interaction among filler, fibres, CPAM, and bentonite played a leading role. It can be assumed that cationic polyelectrolyte was adsorbed on all the components (*i.e.* in our case, the fibers and lime sludge), thus providing anchoring sites for bentonite, which then acted as a bridge between the fibers and lime sludge. Thus, the tenacity of lime sludge attachment to fibers was stronger than a simple CPAM bridge. To achieve optimum performance, a given ratio of CPAM addition is required because in the presence of excess CPAM, the bridging ability of bentonite decreases (Alince *et al.* 2001; Cho *et al.* 2009). When cationic starch was equal to 1% or more than 1%, filler retention was affected by the interaction among fibres, fillers, cationic starch, bentonite, and CPAM. As for the sizing efficiency in Fig. 4, a detectable difference in the Cobb value was observed. At 1.0% cationic starch dosage, the Cobb value was decreased as the dosage of CPAM was increased from 0.018% to 0.068%, and then it increased at 0.093% of CPAM. It is generally believed that the addition of fillers harms the sizing effect heavily. With an increasing amount of calcium carbonate filler, the sizing degree of paper will decrease accordingly. That is because the fillers have a large surface area that can consume the AKD sizing agent, and they themselves are not sized, as it is believed that reactive sizes do not react with fillers. However, it was surprisingly found in this research that at the data point, according to Fig. 3 and Fig. 4, at 1.0% cationic starch and 0.068% CPAM, the best sizing degree corresponded to high filler retention of 79.19%. One explanation for this is when the cationic starch was more than 1.0%, it had a distinct effect on the filler retention; cationic starch not only acted as neutralizer of the anionic trash but also acted as retention agent combined with other additives. The filler and also the AKD was retained on the fibres by the retention aids system. Therefore we attained the best sizing degree corresponding to a high filler retention.

Figures 5 and 6 show the filler retention and Cobb value at 0.3% bentonite. As depicted in Fig. 5, from an overall perspective, the filler retention increased with the increase of cationic starch dosage.

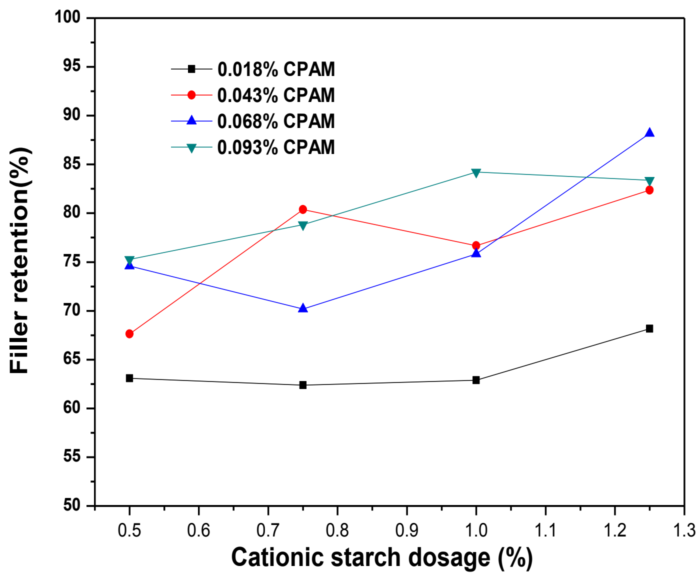

Fig. 5. The influence of the cationic starch dosage on filler retention (bentonite dosage of 0.3%)

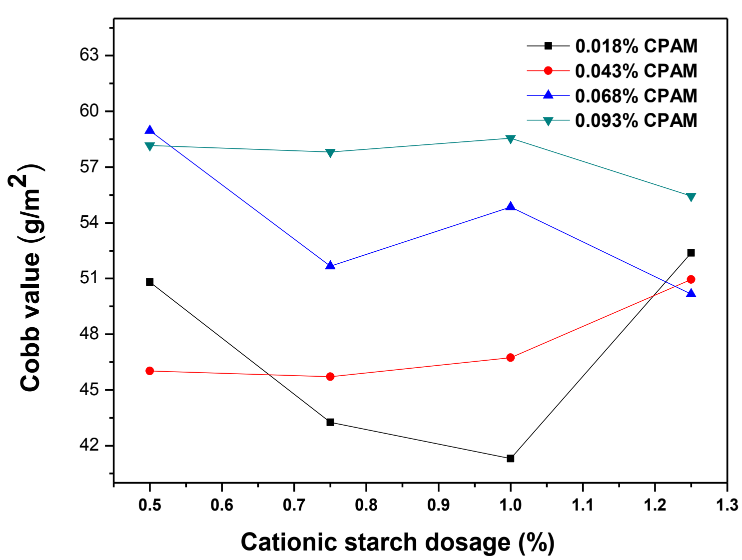

Fig. 6. The influence of the cationic starch dosage on AKD sizing (bentonite dosage of 0.3%)

In a wet end system, cationic starch is commonly added to neutralize the anionic trash and it also acts as retention agent combined with other additives like CPAM. The filler and AKD was retained on the fibres by the retention aids system. Therefore, it is a contradiction for the filler retention and AKD sizing, for filler may deteriorate the AKD sizing. This effect is shown in Fig. 6. When the cationic starch dosage was 1.25%, the Cobb values were approximately 52. As the CPAM and the cationic starch dosage was 0.018% and 1.0%, respectively, the Cobb value was at the lowest point, but at the same time, the filler retention was not that high.

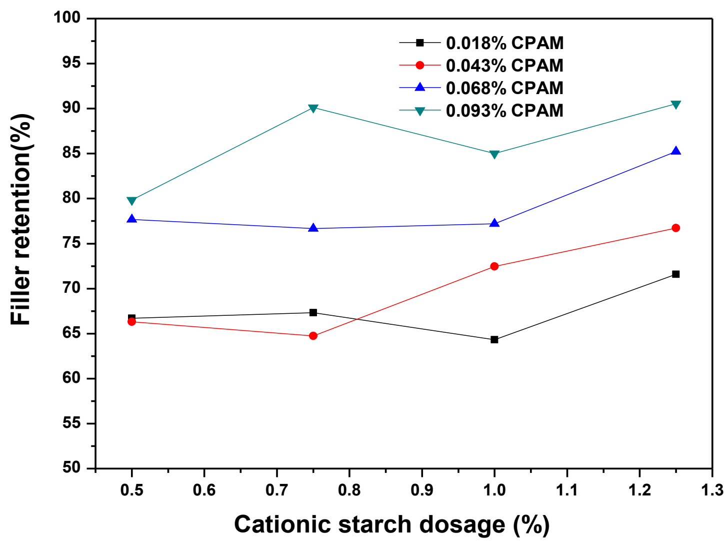

Fig. 7. The influence of the cationic starch dosage on filler retention (bentonite dosage of 0.4%)

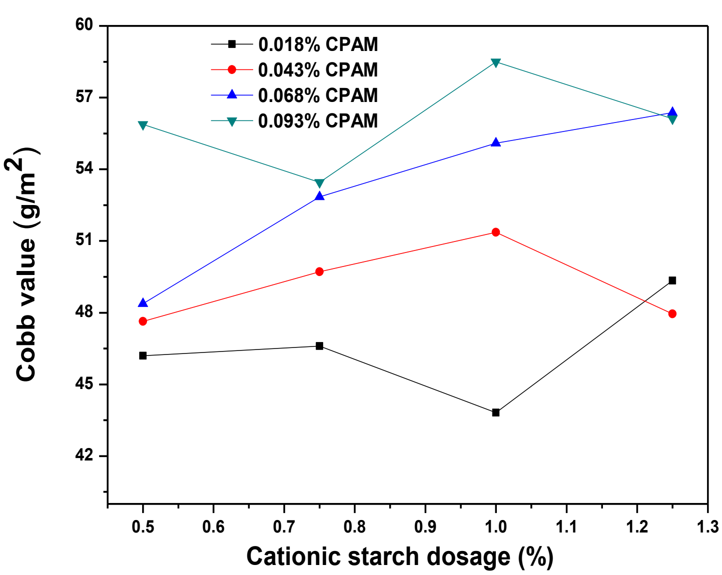

Fig. 8. The influence of the cationic starch dosage on AKD sizing (bentonite dosage of 0.4%)

Figures 7 and 8 show the filler retention and paper Cobb value at 0.4% bentonite. As shown in Fig. 7, the filler showed the same trend as in Fig. 5, indicating that the filler retention increased with the growth of cationic starch dosage. But the functional relationship between retention and starch dosage was flatter. It is assumed that as the bentonite dosage increased, the retention effect of cationic starch became weaker. As for the sizing efficiency in Fig. 8, in contrast to the group with 0.2% bentonite (Fig. 4) and similar to 0.3% bentonite group (Fig. 6), the Cobb value continuously increased as the dosage of CPAM increased from 0.018% to 0.093%.

Figures 9 and 10 show the filler retention and paper Cobb value at 0.5% bentonite. As shown in Fig. 9, filler retention changed little with the increase of cationic starch dosage. Especially when the dosage of CPAM was either 0.068% or 0.093%, the trend was more obvious. As for the sizing efficiency in Fig. 10, Cobb value increased as the dosage of cationic starch increased from 0.5% to 0.75%, and then it decreased from 0.5% to 0.75% of cationic starch. In our experiments, cationic starch were added in the system before AKD to ensure that AKD had retained on the fibres and fundamentally improved the sizing effect. But bentonite and CPAM have some effect on Cobb value, too, so this may result in the interactions among CPAM, bentonite, and cationic starch.

Moreover, as can be seen from Figs. 3 through 10, the filler retention was kept at a high level for 0.068% and 0.093% CPAM loading in the 0.2% and 0.5% bentonite groups. And cationic starch did not show a significant influence on the filler retention until its dosage was up to 1.25%; however, it exerted an obvious effect on the paper's Cobb value.

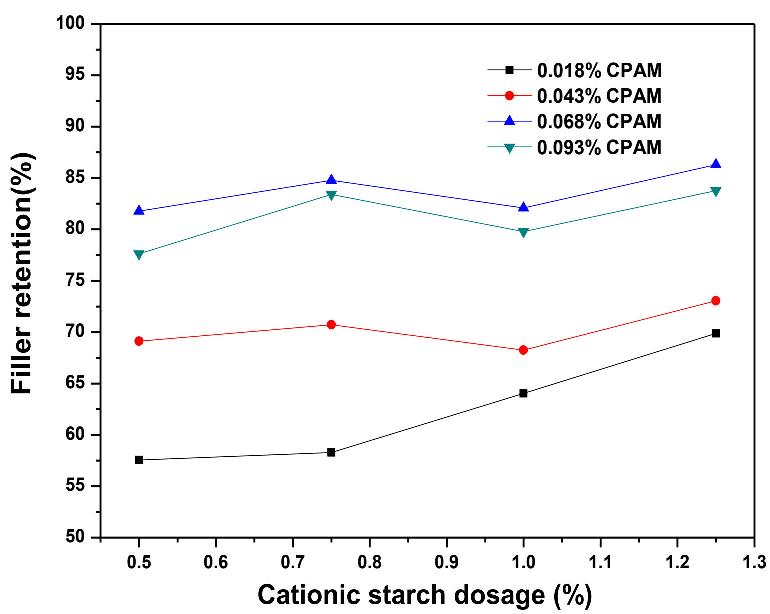

Fig. 9. The influence of the cationic starch dosage on filler retention (bentonite dosage of 0.5%)

On the whole, the desirable Cobb value and filler retention was achieved at 1.0% cationic starch and 0.068% CPAM, 0.75% cationic starch and 0.043% CPAM.

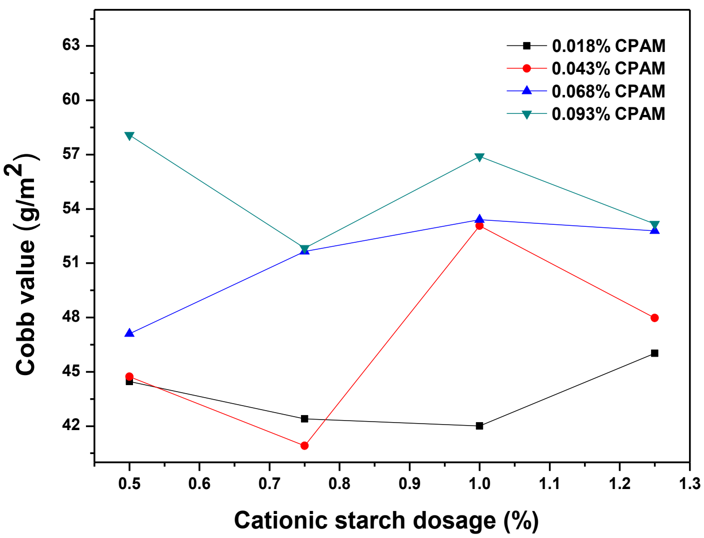

Fig. 10. The influence of the cationic starch dosage on AKD sizing (bentonite dosage of 0.5%)

Figures 11 and 12 show the results as a function of bentonite. In both furnish groups, a relative lower Cobb value and higher filler retention were achieved at a bentonite dosage of 0.2% and 0.3%, respectively. From Fig. 11 it can be seen that as the bentonite dosage increased, the filler retention was decreased gradually. Although it was increased as bentonite dosage was more than 0.4%. The Cobb value was depressed, and the sizing effect was also damaged with the increase of bentonite. As for 0.75% cationic starch and 0.043% CPAM in Fig. 12, as the filler retention was decreased, the sizing effect also became worse. When the bentonite dosage was more than 0.4%, the filler retention and sizing efficiency were then improved. From the results, it can be concluded that fillers as well as AKD retention can be improved due to the improved flocculation with the right bridging function of bentonite, resulting in a balance of the sizing efficiency and filler retention (Cho *et al.* 2010).

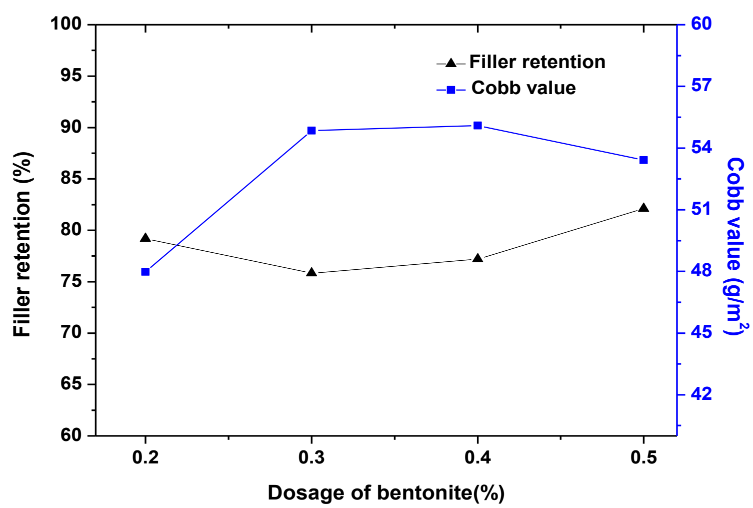

Fig. 11. The influence of the bentonite dosage on the filler retention and Cobb value (cationic starch dosage of 1.0% and CPAM dosage of 0.068%)

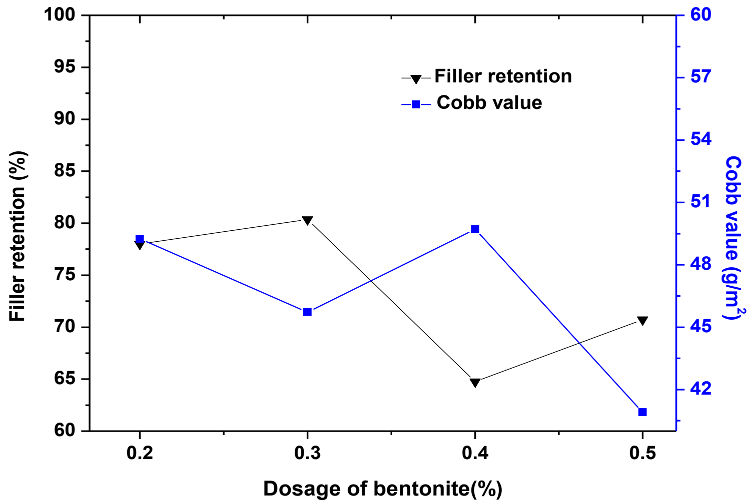

Fig. 12. The influence of the bentonite dosage on the filler retention and Cobb value (cationic starch dosage of 0.75% and CPAM dosage of 0.043%)

CONCLUSIONS

1. Lime sludge was shown to have a more severe negative influence on AKD sizing than PCC. The sizing efficiency lime sludge-filled paper decreased sharply with increasing filler loading. To obtain the same sizing degree, the AKD dosage needed in lime sludge filled paper was twice as much as that in PCC filled paper. For lime sludge has wider particle size distribution, higher specific surface area and larger pore size than commercial PCC (Table 2), and consumes more AKD sizing agent. So in a lime sludge-filled paper system, the retention of AKD was far more important.
2. In the wet end system, cationic starch not only acted as an anionic charge neutralizer, but it also acted as a retention agent. It showed a more significant influence on paper Cobb value than the filler retention. The retention of lime sludge was significantly influenced by CPAM. The filler retention overall increased as the dosage of CPAM increased, due to the bridging function of retention aids system. To get a good sizing as well as filler retention, a lower bentonite dosage was acceptable.
3. At 0.75% cationic starch, 0.043% CPAM, and 0.3% bentonite, a substantial high sizing efficiency of Cobb value (45.72 g/m^2) and filler retention (80.37%) were achieved simultaneously, induced by the synergetic function of the cationic starch/CPAM/bentonite retention aids system.

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