APPLICATION OF CATIONIC MODIFIED CARBOXYMETHYL STARCH AS A RETENTION AND DRAINAGE AID IN WET-END SYSTEM

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Waxy maize contains nearly 100% of the branched amylopectin type of starch, which has a similar structure to that of a commercial anionic organic micro-particle (OMP). It was found that the maize starch would have the same function as the OMP if carboxymethyl groups were introduced; moreover, the performance of carboxymethyl starch as a retention and drainage aid could be enhanced by grafting some cationic groups on the backbone of the starch so that it could absorb on fibers through electrostatic attraction. In this study, the introduced groups of cationic-modified carboxymethyl starch (CCMS) prepared from waxy maize were determined by FT-IR and ^{1}H NMR spectroscopy. Factors affecting retention and drainage, comparison between CCMS and OMP systems, and also the strengthening effect of CCMS were studied. The results showed that CCMS had excellent performance when it was used with cationic polyacrylamide (CPAM) as a retention system. Compared with the OMP, CCMS had better retention performance when the dosage was in the range from 0.01% to 0.08%, and it yielded much more uniform formation of the handsheets. Additionally, CCMS had a strengthening effect on the paper, which distinguished it from other retention aids.

Keywords: Waxy maize; Polyflex; CCMS; Comparison; Retention and drainage; Strengthening effect

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INTRODUCTION

In the early days of papermaking, common retention aids were mainly based on alum, which is able to neutralize the charges on the furnish components, thus allowing attractive forces to dominate so that the furnish components can become flocculated. Due to poor shear resistance of the flocs formed by this mechanism and a narrow maximum in retention versus added chemicals (Scott 1996), single-polymer systems were introduced, based on such chemicals as poly(ethylene imine) (PEI) and cationic polyacrylamide (CPAM), with patching or bridging as the dominant mechanisms (Liu 2010). In recent years, however, the accumulation of anionic trash has become an increasingly important issue, along with the development of papermaking technology. The accumulation of anionic colloidal materials in the wet end tends to impair the effect of retention aids, especially the single-polymer systems (Bley 1992; Wang 2001). In an effort to overcome such problems, dual-polymer systems including treatment with a cation donor such as poly(dimethyl diallyl ammonium chloride) (PDMDAAC), a cationic polymer of low charge density and high molecular weight, were introduced and have become more and more popular since the 1980s. However, most of the traditional dual-polymer systems could cause significant decreases in paper's formation uniformity, particularly at high dosages or when hydrodynamic shear forces were inadequate to break up the resulting flocs (Hubbe 2007). In view of this, traditional single-polymer systems and dual-polymer systems were not ideal for modern high-speed paper machine systems, in which drainage, retention, and formation parameters should be fully controlled (Vishtal *et al*. 2011).

Nano- and micro-particle retention and drainage systems follow a complex flocculation mechanism. Since their introduction to the market, these systems have demonstrated many unique advantages (Wågberg *et al*. 1996; Zhang and Hu 2001; Åsselman and Garnier 2001; Vishtal *et al*. 2011) that the other retention and drainage systems don't possess. Their usage has become increasingly widespread in recent years. At present, the commonly used microparticle retention systems include the Compozil® (Eka Nobel) system consisting of colloidal silica and cationic starch or CPAM, the Hydrocol® (developed by Allied Colloids) system consisting of modified bentonite and CPAM, and the Hydrosil system consisting of aluminium hydroxide and cationic starch (Main and Patrik 1999).

As a natural polymer, starch is comprised of α-D-glycopyranose units, and cellulose from β-D-glucopyranose units. Thus the two materials have a natural affinity for each other. In particular, modified starch, such as cationic and amphoteric starches, has been found to be able to form ionic bonds between cationic groups in the starch derivatives and carboxyl groups in the pulp fibers and fines (Malton *et al*. 1998) and give the paper many excellent properties. Consequently, though starch is known to be added for strength enhancement of paper, an appropriately modified starch can provide the additional benefit of performing as a retention aid (Sang *et al*. 2011). In addition, starch is also considered a sustainable material, featuring complete biodegradability, a wide range of source materials, low cost, and environmentally friendly character (Silva *et al*. 2008; Belhassen *et al*. 2011). Carboxymethyl starch (CMS) is a modified starch that has been widely used in industries, especially in the paper-making industry, and it has broad development prospects for future applications. CMS itself can provide good retention and drainage levels for fiber fines and fillers when applied in pulp furnishes, especially in non-wood pulps, which contain much more fiber fines, and the retention effect tends to improve as the degree of substitution increases. In the present study, the aim was to further treat the CMS to make it cationic, and therefore, the cation groups of CMS could adsorb more fiber fines and fillers through electrostatic force and exhibit stronger retention and drainage effects, without increasing the anionic trash. Gelatinized waxy maize starch with 83% of branched amylopectin (structure similar to the organic micropolymer, OMP) was explored as the raw material, and chloroacetic acid was used as anionic etherification agent for converting the carboxy of the water-soluble gelatinized waxy maize to the carboxymethyl form. Thus the waxy maize was turned into CMS, then CCMS was prepared by using cationic etherification agent to make a cationic version of CMS. Thus, cationic modified carboxymethylated starch (CCMS) was evaluated as a component in a retention aid system, for which it would take the place of, and possibly function similarly to, the anionic particles used in the conventional microparticle retention systems.

CCMS is a type of natural macromolecule that can be used with CPAM as a retention aid in the microparticle retention and drainage system. Moreover, the macromolecules bear a certain number of free hydroxyl groups along the starch backbone.

These hydroxyl groups are capable of forming hydrogen bonds with those of the cellulose and hemicellulose polymers present at the surface of the fibers. Besides, they can increase the number of naturally formed hydrogen bonds in the bonded areas between the fibers, as well as improve the retention of the fiber fines. Consequently, CCMS also has the function of strengthening the paper, in addition to its role as a retention and drainage agent.

EXPERIMENTAL

Materials

CCMS was prepared in our lab (carboxyl methyl group DS 0.7 and cationic group DS 0.012). The waxy maize was supplied by National Starch. CPAM (molecular weight 5 million, medium charge density) was supplied by Ciba Chemicals (Pecol 47). Bleached eucalyptus kraft pulp with 38ºSR beating degree used in this study was obtained from Brazil. The ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) were supplied by APP Golden East Paper. The sodium chloride and calcium chloride were both analytical grade commercial products (Shanghai Chemical Reagent Factory, China).

Methods

Preparation of CCMS

The waxy maize starch was added into a four-neck round bottom flask, along with isopropyl alcohol, and the mixture was allowed to stir and heat in the water bath. Then the alkalization reaction proceeded after adding NaOH solution into the mixture. After the alkalization reaction, the mixture in the flask was heated again to a specified temperature. Then the carboxymethylated reaction was carried out after the addition of chloroacetic acid solution and isopropyl alcohol. NaOH was added into the flask to adjust the pH to *ca.* 11 after the selected period of reaction. Then the cationic reaction was started by trickling cationic etherification agent at controlled flow rates for 2 to 5 hours.

FT-IR analysis

The dried CCMS powders were embedded in KBr pellets and were analyzed by using a Nicolet IR-360 FTIR spectrometer. The spectra were recorded in the absorption band mode in the range of 4000 to 500 cm^{-1}.

^{1}H NMR analysis

^{1}H NMR spectra of CCMS were measured with a Bruker Avance DRX 500MHz NMR spectrometer using D_2O as the solvent.

Evaluation method of retention and drainage

In this experiment, the CPAM-CCMS retention and drainage system was chosen. CPAM was added first and stirred until the ingredients in the mixture were uniformly mixed, then CCMS was added to flocculate suspended materials in the papermaking system.

Measurement of drainage time

The furnish (1000 mL, total) consisted of 0.2wt% fiber suspension with 25wt% (based on dry fiber) calcium carbonate filler, which were added into a Dynamic Drainage Jar (DDJ), and stirred at the rotational speed of 1500 rpm. The retention aid CCMS with the dosage ranging from 0 to 0.1wt% was added into the furnish at the reduced stirring speed of 750 rpm, and then the drainability of the pulp was measured by using a Canadian Standard Freeness (CSF) tester according to the TAPPI T261 cm-00 standard.

Measurement of retention

Evaluation of the first pass retention (FPR) was conducted following TAPPI T261 cm-00 standard. A furnish consisting of 0.5wt% fiber suspension (500 mL) was added into the DDJ and stirred at 1500 rpm at first. Then CCMS (dosage was from 0 to 0.1wt%) was added at 750 rpm. The filtrate was collected for the initial 30 s after 10 s from the addition of CCMS. Then, the filtrate was weighed, filtered, dried (105 ^{o}C, 4h) to constant weight, and the ash content was tested (900 ^{o}C, 3h).

Determination of physical properties of handsheets

The handsheets were made with a PTI RK-2A device from Austria. The physical properties of pulp handsheets in this study were determined according to the following TAPPI methods: TAPPI T410 om-02 (basis weight), TAPPI T494 om-01 (tensile strength), TAPPI T414 sp-96 (tearing resistance), TAPPI T511 om-02 (folding endurance), and TAPPI T560 om-05 (whiteness).

RESULTS AND DISCUSSION

Compositional Analysis

Figure 1 presents the FT-IR spectra of CCMS and CMS.

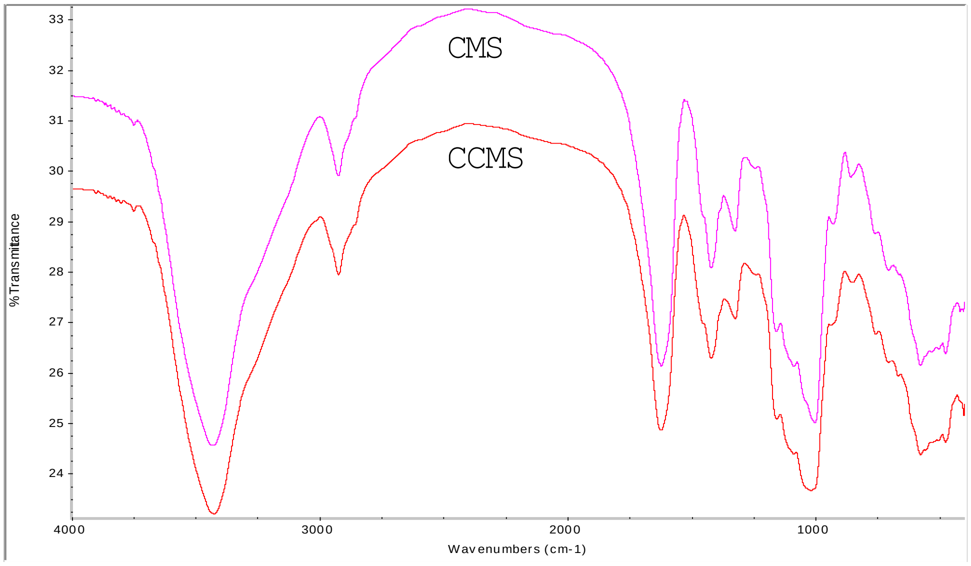

Fig. 1. FT-IR spectrum for CCMS

As can be seen, the spectrum of CCMS was similar to that of CMS with respect to characteristics of the starch peaks. The spectrum of CMS showed a sharp and strong peak at 1623 cm^{-1} that was attributed to the carboxyl group of the CMS structure, and the characteristic absorption bands at *ca*. 1421 cm^{-1} and 1326 cm^{-1} belonged to the coupling of O-H and C-H bending vibrations.

Compared with CMS, CCMS also had absorption bands appearing at 1623 cm^{-1}, 1421 cm^{-1}, as well as 1326 cm^{-1}, which indicated that the starch had been carboxymethylated. The weak stretching vibration of C-N bond was not observed because of overlapping with the strong band of -COO- bonds (1489 cm^{-1}), which suggested the existence of the cationic quaternary ammonium group of CCMS.

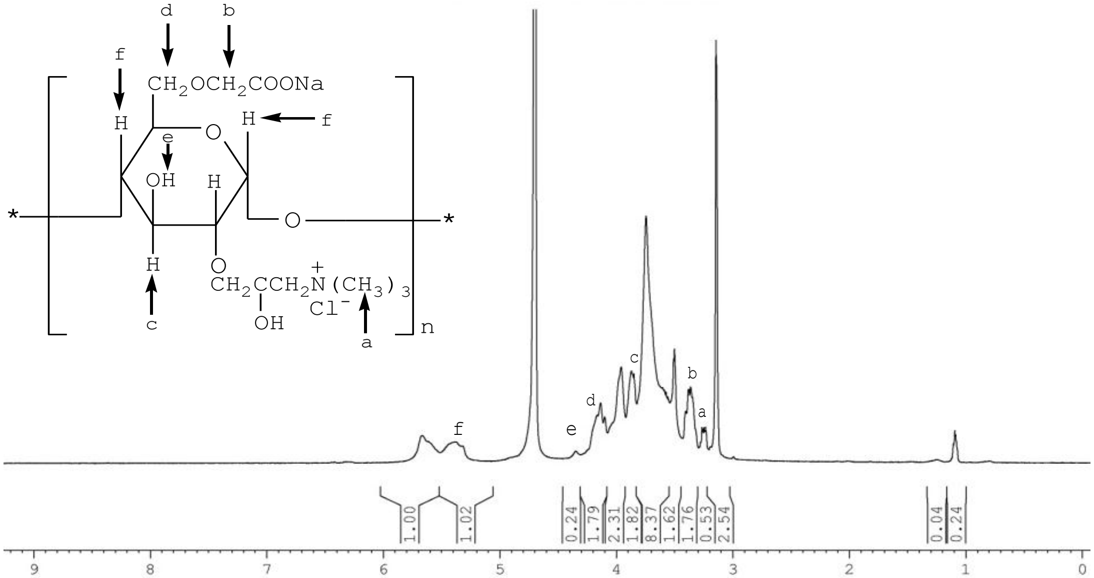

Fig. 2. ^1H NMR spectrum for CCMS

A typical ^1H NMR spectrum of CCMS is shown in Fig. 2. The signal corresponding to the quaternary ammonium group was identified at 3.1 ppm for H-a, which indicated that the CMS had been cationized. The signal at 3.7 ppm implies the H-b in the group of $-CH_2COO-$, whereas the hydrogen of β−C linked with the remaining -OH of the starch appeared as peaks in the range 3.5 to 3.8 ppm. The signals at 3.9 to 4.1 ppm correspond to the methylene hydrogen linked with the carboxymethyl ether structure. The remaining –OH groups of glucose appeared at 4.7 ppm. The signals at 5.3 ppm and 5.6 ppm may correspond respectively to the hydrogens of the carbons in positions 4 and 1.

Figure 3 shows a three-dimensional molecular model for CCMS, *i.e.* a visual representation of an ideal macromolecule structure of CCMS derived from the basic starch. In this model, hydroxyl groups are the active centers of the macromolecule of starch. These active centers not only can be carboxymethylated, but they also can be cationic-modified, which results in a modified and multifunctional starch. Each starch macromolecule in this idealized model is comprised from numerous α-D-glycopyranose units, and each α-D-glycopyranose unit has hydroxyls in different positions of the ring. Therefore, the carboxymethylated and cationic-modified reactions are supposed to appear in different positions in theory.

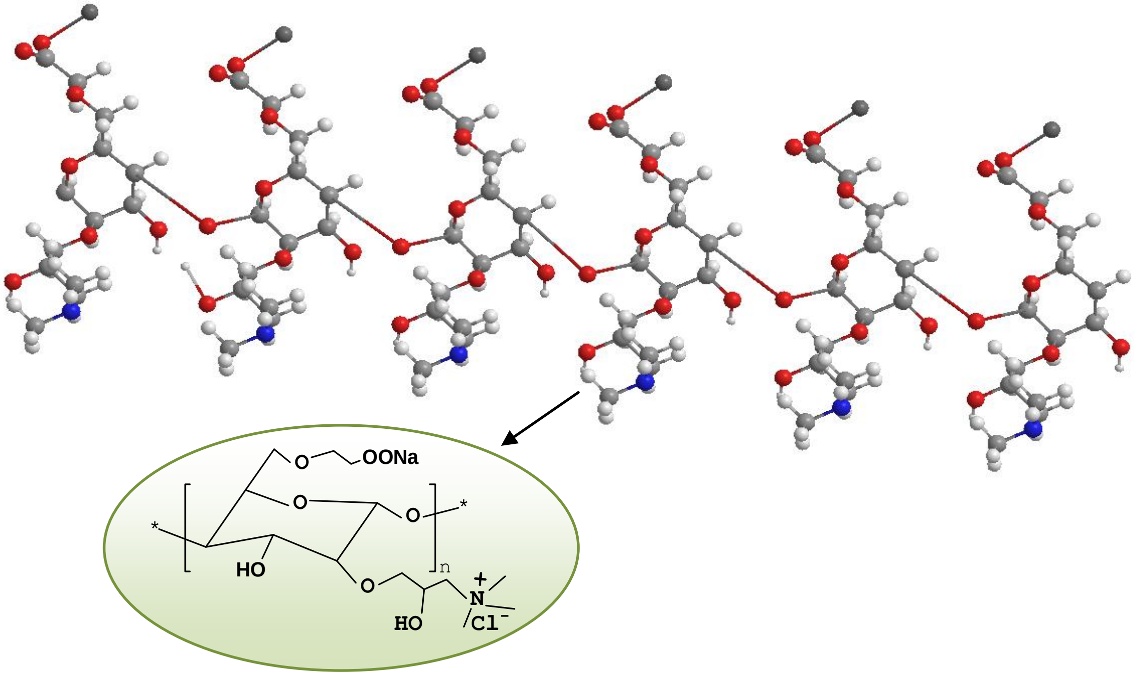

Fig. 3. Molecular model of CCMS

Factors Affecting Retention and Drainage

Effects of the dosage of CPAM on retention and drainage

Retention and drainage results are shown in Fig. 4 as a function of CPAM dosage.

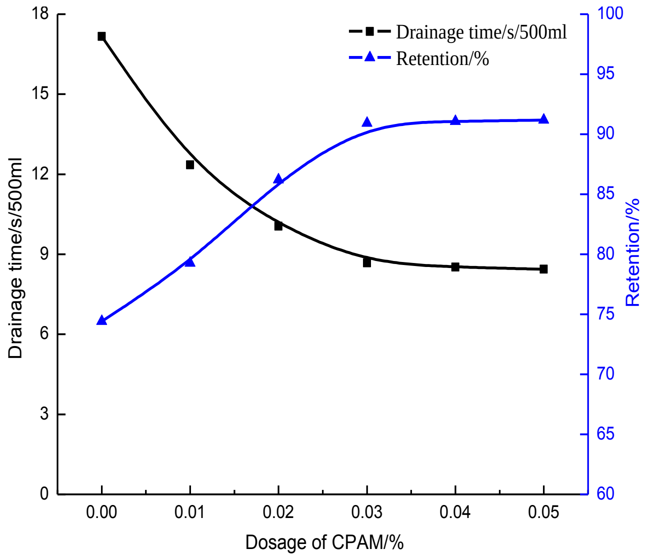

Fig. 4. Effects of dosage of CPAM on drainage time and retention

When a certain dosage of CPAM was first added to the pulp, it flocculated with the anionic fibers, and then the flocs were broken up to form cationic patches by hydrodynamic shear. Whether it could satisfy the need of CCMS, which carried high negative electric charge, and form the micro-flocculation depended on the dosage of CPAM. In this experiment, the dosage of CCMS and GCC were kept constant at 0.075wt% and 25wt%, respectively, and the results are shown in Fig. 4 as a function of the dosage of CPAM.

Figure 4 shows that as the dosage of CPAM increased, the drainage time was reduced rapidly at first, then barely reduced further when the dosage exceeded 0.03wt%, which demonstrated that the drainage performance became better after adding CPAM, and the optimum was 0.03wt%. The retention of fines in the sheet also was improved with the increasing dosage of CPAM. When the dosage of CPAM was over 0.03wt%, the retention performance tended to be saturated and stabilized. So in the CPAM-CCMS system, under the precondition of the dosage of CCMS 0.075wt%, the optimum dosage of CPAM was judged to be 0.03wt%.

Effects of the dosage of CCMS on the performance of retention and drainage

In order to evaluate the effect of the dosage of CCMS on the performance of retention and drainage, the dosage of ground calcium carbonate (GCC) and CPAM was kept constant, at 25wt% and 0.03wt%, respectively. Just the dosage of CCMS was varied. The results are shown in Fig. 5.

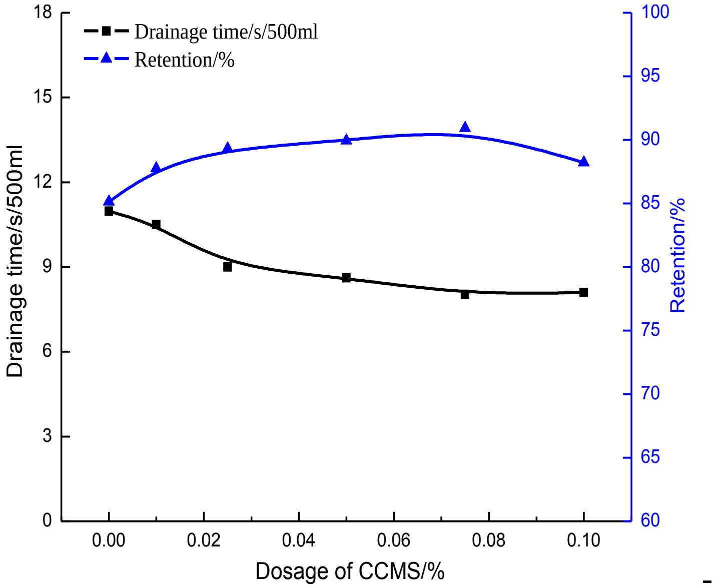

Fig. 5. Effects of dosage of CCMS on drainage time and retention

As shown in Fig. 5, with the dosage of CCMS increasing from 0 to 0.1wt%, the retention was increased and the drainage time was reduced. The drainage time tended to stabilize as the dosage of CCMS was increased above 0.075wt%. Therefore, the optimum dosage of CCMS was close to 0.075wt%. At this optimum point, the drainage time was the shortest, *ca*. 8 s. Besides, the retention also increased gradually. But the increasing trend started to reverse when dosage of CCMS was above 0.075wt%. When the dosage level of CCMS was at 0.075wt%, the retention reached its largest value of 90.9%. One possible reason was that CCMS could form a micro-flocculation system with pulp, which absorbed cationic polymer (CPAM), and therefore, the specific surface area of the pulp was reduced. Another possible reason was that CCMS is a water-soluble cationic polymer which has many hydroxyl groups and high content of carboxymethyl groups, so CCMS contributes to a large water retention value. Consequently, when the dosage of CCMS was in excess, it would be expected to damage the retention and drainage performance.

Effects of hydrodynamic shear stress on the performance of retention and drainage

Under different running speed and different flowing conditions, the intensity of shear stress may have different impacts on the components of fines and microparticles in the paper stock, and thus influence the performance of drainage and retention. In recent years, with increases in the running speeds of paper machines, the hydrodynamic shear stress also has tended to increase gradually, which has tended to increase the shear force applied to the stock. In this experiment, the dosage of GCC was 25wt%, the dosage of CPAM was 0.03wt%, and the dosage of CCMS was 0.075wt%. Shear stress was variable. Experimental results are shown in Fig. 7.

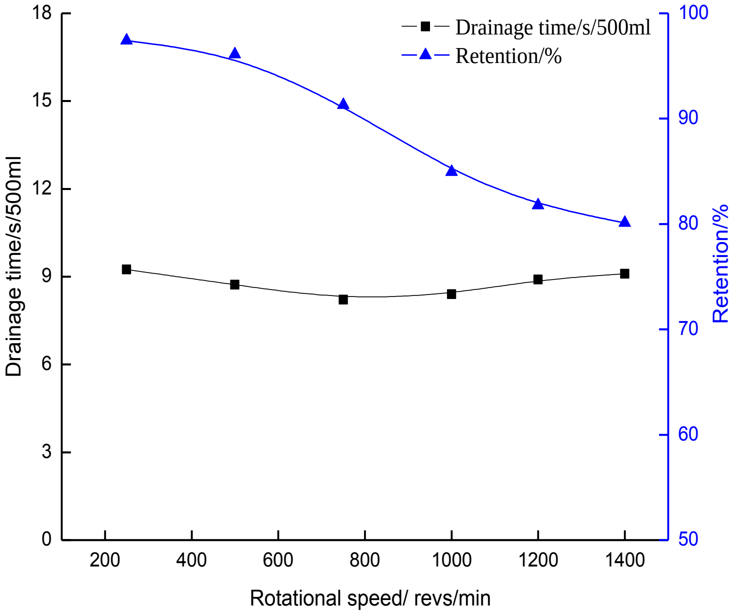

Fig. 6. Effects of rotational speed on drainage time and retention

As shown in Fig. 6, hydrodynamic shear had little effect on the drainage performance, as we can see that the drainage time barely changed as the rotational speed increased. Figure 6 also shows that the retention of sheet decreased with increasing shear. When the rotational speed was 250 revs/min, the retention of sheet was close to *ca*. 98%. As the rotational speed increased to 1400 revs/min, however, the retention decreased to *ca*. 80%. Consequently, it could be concluded from the experiment that shear intensity had little impact on the performance of drainage, but it impaired the retention of fines in the sheet significantly if the shear stress was too high.

Effects of electrical conductivity on the performance of retention and drainage

Electrolytes can hinder various effects related to the charges of fibers surface, as well as weaken the attraction between CCMS and fibers. The concentration of electrolytes can be monitored by electrical conductivity. Swerin *et al*. (1993) explored the effect of electrolytes in a CPAM system, and they showed that the higher the electrical conductivity, the more the groups of positive charges of CPAM and the groups of negatives charge of other materials were shielded, and therefore it prevented the other materials from adsorbing on CPAM as effectively. At a sufficiently high conductivity, the system eventually lost performance in terms of retention and drainage.

The impact of electrical conductivity on retention and drainage performance of CCMS was investigated under the following conditions: the dosage of CPAM was 0.03wt%, the dosage of CCMS was 0.075wt%, and the dosage of GCC was 25wt%. Electrical conductivity was adjusted by NaCl, $CaCl_2$, and a mixture of NaCl and $CaCl_2$ (Na^+:Ca^{2+} = 1:3 mol/mol), respectively. The results are shown in Figs. 7 and 8.

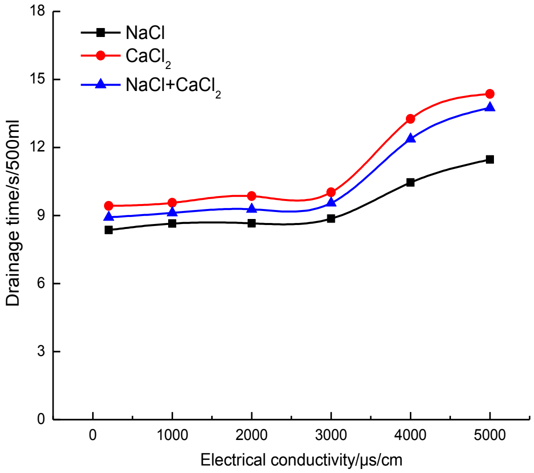

Fig. 7. Effects of electrical conductivity on drainage time

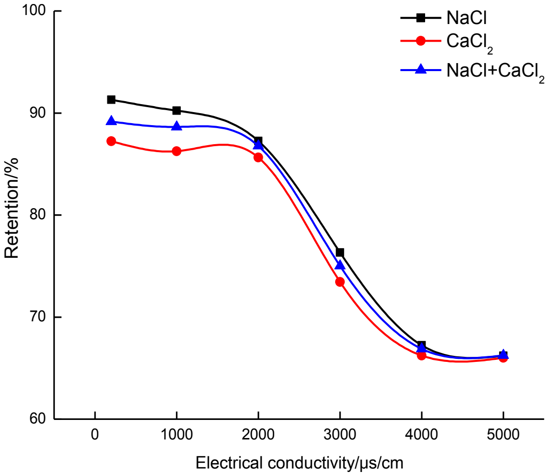

Fig. 8. Effects of electrical conductivity on retention

From Fig. 7, it can be seen that when the electrical conductivity was between 230 and 3000 μS/cm, the increasing of salts content had little effect on drainage time. But as soon as the electrical conductivity was above 3000 μS/cm, the drainage time increased rapidly, which indicated that extra salt decreased the drainage performance. It can also be found that calcium was more detrimental than sodium in the system.

Figure 8 shows that the retention was reduced slowly with the electrical conductivity increasing from 230 to 2000 μS/cm. When the electrical conductivity was in the range of 2000 to 4000 μS/cm, the performance of retention of CPAM-CCMS system decreased linearly with the increasing of electrical conductivity. This demonstrated that under the high electrical conductivity condition, the performance of retention and drainage of CPAM-CCMS system was impaired, as in the case of other retention systems in general. In addition, Figs. 7 and 8 also indicated that the influence of univalent metal ions on the performance of retention and drainage was less than that of multivalent metal ions.

Comparison between CCMS and OMP for the performance of retention and drainage

The performance of retention and drainage of both CCMS and OMP was studied and compared in this experiment. In this experiment, the dosage of CPAM was kept constant at 0.03wt%. The results are shown in Figs. 9 and 10.

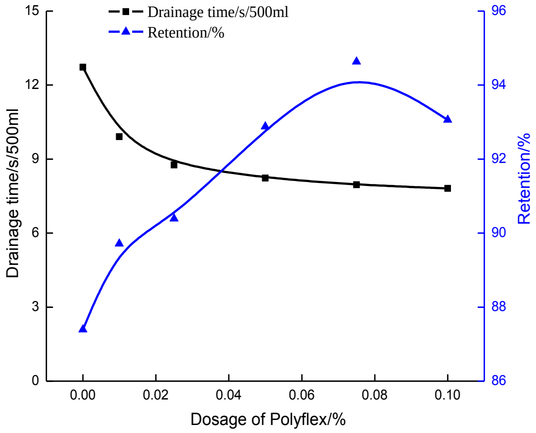

Fig. 9. Effects of dosage of Polyflex on drainage time and retention

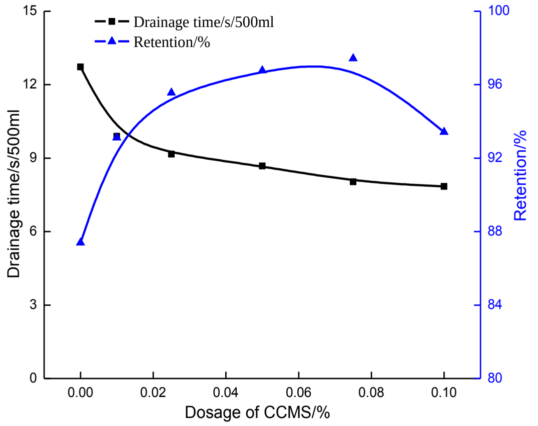

Fig. 10. Effects of dosage of CCMS on drainage time and retention

In the OMP system, as the addition of OMP was increased from 0 to 0.1wt%, the drainability was improved from *ca.* 13 s to *ca.* 8 s, as well as the retention was improved from *ca.* 87% to the highest level of 94.6% when the OMP addition was 0.075wt%. At the same time, CCMS system followed a similar trend as the OMP system, and drainage time was improved monotonically from *ca.* 13s to 8s with the addition of CCMS increasing from 0 to 0.1wt%. The optimum retention of 97.4% was achieved when the dosage of CCMS was 0.075wt%, just the same addition as that of the OMP. However, it is worthy to note that CCMS system had a better retention performance than that of the OMP when the dosage was between 0.01wt% and 0.08wt%.

Influence of CCMS and OMP on the pulp handsheets physical properties

Pulp handsheets were prepared under the conditions of dosage of $CaCO_3$ 25wt%, CPAM 0.02wt% and starch 1wt% in the stock. Basis weight, whiteness, and formation of pulp handsheets were tested, and the results are shown in Tables 1 and 2.

Table 1. Pulp Handsheet Properties Using OMP Drainage & Retention System

Polyflex dosage ％	0	0.01	0.025	0.05	0.075	0.1
Basis weight (g/m^2)	73.06	74.99	75.56	77.65	79.11	77.80
Whiteness（ISO%）	87.88	88.29	88.77	89.06	89.10	88.78
Formation	117.8	104.15	96.6	76.15	82.4	87.8

Table 2. Pulp Handsheet Properties Using CCMS Drainage & Retention System

CCMS dosage％	0	0.01	0.025	0.05	0.075	0.1
Basis weight (g/m^2)	73.06	77.84	79.89	80.89	81.44	78.09
Whiteness（ISO%）	87.88	89.27	89.28	89.30	89.41	89.00
Formation	117.8	106.05	110.3	105.3	108.8	116.85

From Tables 1 and 2, it can be seen that the highest basis weight and whiteness was achieved at the dosage of 0.075wt%, while the best formation was obtained at the dosage of 0.05wt% in both the OMP and CCMS systems. Comparing the physical properties of handsheets using OMP and CCMS as the drainage and retention aids, we could conclude that basis weight was easier to be controlled under the OMP conditions. Meanwhile, both systems had the similar whiteness performance, but the formation performance of OMP system, as we could see, was much better than that of CCMS system.

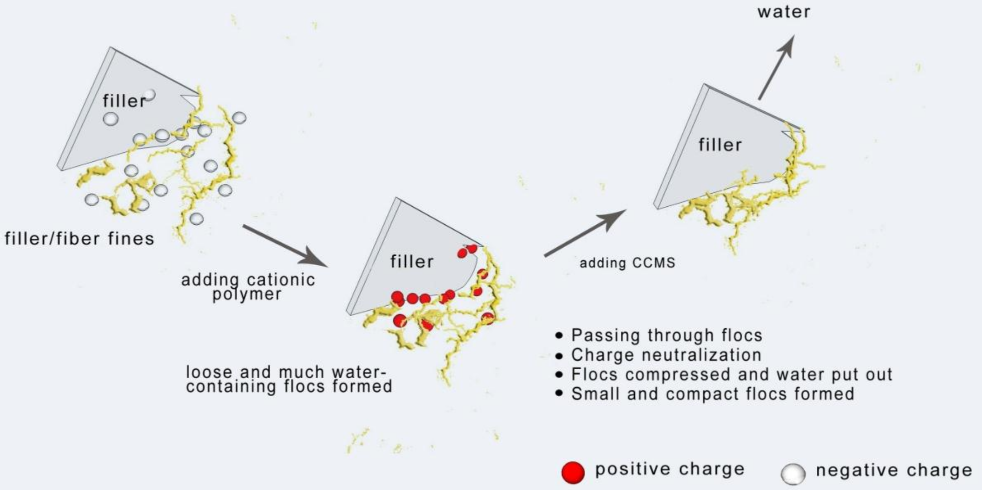

Fig. 11. Microparticle system by adding CCMS

Strengthening Effect of CCMS

The strengthening effect of CCMS to pulp handsheets was evaluated by the addition of 25wt% PCC and 0.03wt% retention aid CPAM. The dosage of CCMS varied in the range of 0 to 1%. (All the dosages above are based on dry fibers). The strength properties are shown in Table 3.

Table 3. The Effect of Dosage of CCMS on Strengthening

CCMS dosage ％	0	0.05	0.1	0.5	1
Tear index/ mN*m^2/g	4.23	4.43	4.72	5.81	5.9
Tensile index/ N*m/g	34.19	35.83	40.64	43.91	47.49
Folding number/times	7	8	12	19	22
Basis weight (g/m^2)	46.05	57.74	58.76	58.09	62.05

As shown in Table 3, all the strength indicators of the pulp handsheets improved with increasing dosage of CCMS, and the tensile index and the folding number improved in a wider scope. When the dosage level of CCMS rose from 0 to 1.0wt%, the tensile index increased from 34.19 N·m/g to 47.49 N·m/g, representing an enhancement by 38.9%. At the same time, the folding number was improved by 13, rising from 7 times to 20 times. The tear index increased from 4.23mN·m^2/g to 5.9 mN·m^2/g, and the relative increase was 39.48%. With the further addition of CCMS (data not shown), the strengthening effect began to become worse, and meanwhile, the retention rate of the pulp followed a decreasing trend, which may has something to do with the high anionic substitution degree of the CCMS. Because CCMS showed negative performance when used alone, too high dosage facilitates the dispersion of paper stock instead of strengthening and retention, resulting in the decreasing retention of CCMS in the paper stock. Consequently, the proper dosage of CCMS as strengthen agent in the wet-end needs to be controlled within 1wt%.

CONCLUSIONS

1. For a CPAM-CCMS system, when the dosage of CPAM was 0.03wt% and the dosage of CCMS was 0.075wt%, the optimum retention and drainage performance was achieved.
2. Hydrodynamic shear stress had little effect on the drainage performance; however, it impaired the fine-particle retention noticeably, especially under the condition of very high shearing strength. When electrical conductivity was above 3000 μS/cm, the performance of retention and drainage was reduced rapidly with increasing electrical conductivity. Furthermore, the effect of calcium ions was more obvious than that of sodium ions.
3. Compared with an organic micropolymer (OMP) system, the retention performance of CCMS-CPAM was better and increased by 2.8% when the dosage ranged from 0.0wt1% to 0.08wt%. The varying trend of the drainage time of the two systems was similar.
4. The pulp handsheets prepared under CCMS conditions had much better formation performance than that under OMP conditions, while whiteness was more easily controlled by the latter.
5. Apart from retention and drainage performance, CCMS also had a strengthening effect on paper, which distinguished it from the ordinary retention aid systems. When the dosage of CCMS was controlled within 1wt%, the strength indexes of pulp handsheets was improved by a certain extent, especially the tensile index and the folding number, which were improved by 38.9% and 13, respectively.

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