

## **CATIONIC MICROPARTICLE RETENTION AIDS: THE MECHANISM STUDY AND LABORATORY EVALUATION**

Hiroshi Ono<sup>†</sup> and Yulin Deng<sup>\*</sup>

Institute of Paper Science and Technology, 500 10th Street, N.W., Atlanta, GA  
30318

### **ABSTRACT**

The cationic polymeric microparticles (CPMP) with different charge densities and particle sizes were synthesized and characterized. The flocculation and retention of precipitated calcium carbonate (PCC) and titanium dioxide (TiO<sub>2</sub>) suspensions induced by a cationic polymeric microparticle retention system were studied in both the original and washed pulps. For the dispersion of PCC in the washed pulp, the CPMP alone is not an effective retention aid because both the CPMP and PCC are positively charged. However, the retention of fillers can be significantly enhanced by dispersing PCC in an unwashed pulp. The combination of CPMP and a high-molecular weight, water-soluble polymer led to excellent retention of PCC. Although both anionic or cationic polymers can be used in conjunction with CPMP, different mechanisms are involved in these dual-retention systems. For the dual-retention system of CPMP-APAM (anionic polyacrylamide), it is believed that a bridge is formed between the CPMP patch and APAM. In contrast to the CPMP-APAM system, the increase in the filler retention efficiency by the dual-retention system of

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<sup>†</sup>: Present address: Central Research Laboratory, Nippon Paper Industries Co. Ltd., 5-21-1, Oji, Kita-ku, Tokyo 114, Japan.

<sup>\*</sup>: To whom correspondence should be addressed.

CPMP-CPAM (cationic polyacrylamide) is not through the bridging formation between CPMP and CPAM, but is caused by the configuration change of the cationic polymer in the presence of CPMP. It is believed that the pre-adsorption of CPMP can prevent CPAM from getting flat on the solid surface, resulting in an extended polymer conformation and high retention efficiency. It has also been found that the particle size of a cationic polymeric microparticle is a critical factor affecting the PCC retention.

## INTRODUCTION

In the past decades, wet-end operations have been dramatically changed mainly because of the shift from acid to alkaline papermaking, greater use of high-yield and recycled pulp, and faster machine speeds. Because of these changes, many new retention systems, such as dual retention, microparticle retention, and micropolymer retention [1-5], have been brought into the paper industry. Although these new systems may greatly improve first-pass retention and paper formation for fine paper grades, they are less effective for high-yield pulps containing large amounts of dissolved and colloidal anionic substances. Therefore, development of new retention systems that can achieve a high first-pass retention and reduce the total cationic demand simultaneously is desired by the paper industry.

It has been known that both the flocculation kinetics and thermodynamic processes will affect the floc formation when a cationic polymer is used as a flocculant or retention aid. The most important kinetic properties are the rate of the adsorption and the initial conformation of adsorbed polymer. The loop length of polymer on a solid surface is a critical factor affecting the bridging flocculation because an effective flocculation can be obtained only when the loop length of adsorbed polymer is long enough to overcome the repulsion force between two charged particles. This suggests that, as an effective bridging flocculation, (1) the polymers must be adsorbed on the suspension surface, and (2) the loops of adsorbed polymer molecules must be long enough. The former requires a high charge density of polyelectrolyte to generate strong attractive forces between polymers and particles, and the latter requires a low charge density of polyelectrolyte to form extended polymer loops. The conflict of requirements between (1) and (2) suggests that the polymer must have an optimized charge density if it is used as an effective flocculant. Both theoretical calculation [6] and experimental studies [7-9] indicated that high charged polymers adsorb in a flat

conformation rather than an extended polymer chain. In contrast to a water-soluble polymer, there is no conformation change when a cationic microparticle adsorbs on a negatively charged substrate [10-12].

As reported previously [13], the cationic polymeric microparticle was proved to be an effective flocculate for negatively charged PCC suspension, and the flocculation efficiency could be further improved by addition of an anionic water-soluble polymer. It was also found that the addition order of CPMP and anionic water-soluble polymer could affect the flocculation efficiency. However, all of the flocculation data in our previous study [13] were measured in a static rather than a dynamic condition. In this study, therefore, the performance of a cationic polymeric microparticle as a retention aid for PCC and  $\text{TiO}_2$  in both the presence and absence of a water-soluble polymer was examined by Dynamic Drainage Jar (DDJ), and the effect of the surface charge and size of the cationic polymeric microparticle, addition order, pH, and surfactant content on the filler first-pass retention was examined. Then, the efficiency of patching formation of CPMP was compared with a conventional cationic coagulant, polyDADMAC. The retention mechanism using the CPMP-CPAM dual retention system was discussed.

Potentially, a cationic polymeric microparticle have advantages over a water-soluble polyelectrolyte when it is used as a retention aid or co-retention agent because: (1) there is no conformation change when the CPMP adsorbs onto a negatively charged substrate, which results in a more effective patch formation; (2) the bridge length can be exactly controlled by particle size; (3) the total cationic demand of the pulp furnish in papermaking can be reduced; (4) the cationic microparticles do not penetrate into the pores of the fiber surface due to their inflexible structure; and (5) there is no accumulation of microparticles in a closed white water system because of the strong bonding force between CPMP and negatively charged substances. Although the combination of a cationic polyelectrolyte with an anionic microparticle, such as bentonite and silica [14-17], has been widely used in the paper industry as a retention aid, the combination of a cationic polymer with a cationic microparticle has not been studied in the scientific literature except for one patent [18] that claimed the dual system of silica sol and cationic polyacrylamide can be an effective retention aid for papermaking. It will be interesting to see if the combination of a cationic polymer with CPMP can be an effective papermaking retention aid. In this study, the cationic polyelectrolyte was combined with CPMP as a dual retention aid, and the retention efficiency was studied. The mechanism of this novel system was also suggested.

## MATERIALS AND METHODS

### Materials

Styrene (Aldrich Chem.) was distilled to remove inhibitors before polymerization. Divinylbenzene (DVB, Aldrich Chem.) was used as a crosslinker. Two types of initiators, 2,2'-azobis(N,N'-dimethylene-isobutylamidine) dihydrochloride (VA-044, Wako Pure Chemicals) and potassium persulphate (KPS, Aldrich Chem.), were used for cationic and anionic polymeric microparticle preparations, respectively. In the preparation of CPMP, a cationic surfactant, cetyltrimethyl-ammonium bromide (CTAB, Aldrich Chem.), was used as an emulsifier, and in the preparation of an anionic polymeric microparticle (APMP), an anionic surfactant, sodium dodecyl sulfate (SDS, Aldrich Chem.), was used.

The physical properties of water-soluble polymers are given in **Table 1**. In order to study the effect of polymer charges on the retention efficiency in a CPMP dual retention system, a polymer that has the same molecular weight but an opposite charge with Percol®175 (Allieds Colloid) was prepared by hydrolysis of Percol®175. The hydrolysis was carried out in a 1-M NaOH solution at room temperature for more than 2 hours. Because the hydrolysis will only reduce the cationicity but not affect the chain length of the polymer backbone [19], the hydrolyzed Percol®175 (abbreviated as A175) should have the same molecular weight as original cationic Percol®175 (abbreviated as C175), but the former was anionically and the latter was cationically charged. The charge density of C175 and hydrolyzed A175 obtained by colloid titration was +900 and -550  $\mu\text{eq/g}$ , respectively.

The cellulosic fibers used were once-dried bleached softwood kraft pulp (BSK). Clean fibers were prepared by washing the pulp three times using deionized water. The absence of colloidal and soluble polymers in pulp was confirmed by colloidal titration of the pulp supernatant.

Precipitated calcium carbonate (PCC, Specialty Minerals Inc.) was a scalenohedral calcite filler product (ALBACAR HO®) with an average particle size of 1.3 micron and specific surface area of 12  $\text{m}^2/\text{g}$ . Titanium dioxide (Aldrich Chem., anatase, 99.9+%) was used as received. The particle size of  $\text{TiO}_2$  was 266 nm with a standard deviation of 38% (dynamic light scattering). A scanning electron micrograph showed that the particles were not uniform spheres.

Sample	Symbol used in this study	Chemical composition	Molecular weight	Charge density
Percol®175	C175	cationic PAM	very high	+900 µeq/g
Hydrolyzed Percol®175	A175	hydrolyzed cationic PAM	very high	-550 µeq/g
Percol®172	A172	anionic PAM	medium high	medium anionically charged

**Table 1.** Physical properties of water-soluble polymers used in this study.

When a negatively charged PCC was needed, the PCC was first modified by an anionic polyacrylamide before it was added into the pulp suspension. To prepare anionic polyacrylamide-pretreated PCC, a medium-charged anionic polyacrylamide (1% based on the weight of PCC) with a molecular weight of 200,000 g/mol was first added into the PCC suspension. After adsorption equilibrium, the PCC particles were removed by centrifugation then washed with deionized water leaving only strongly bonded APAM on the PCC surface. Finally, the PCC was dried at ~ 150 °C. The anionic polyacrylamide-pretreated PCC showed a strong negative charge and formed a relatively stable dispersion in water.

### Preparation of CPMP

The cationic polymeric microparticles with various particle sizes and charge densities were prepared according to the method described by Goodwin et al. [20]. A typical example of polymerization (sample D in **Table 2**) was described as follows: a 250-ml double-wall glass reactor equipped with a mechanical stirrer was filled with 150 ml of deionized water, 108 mmol of styrene, 8.2 mmol of cationic surfactant, and 4.3 mmol divinylbenzene. The solution was flashed with nitrogen for 30 minutes to remove oxygen in the solution, then was thermostated at 60 °C. After temperature equilibrium, 6.9 mmol of VA-044 in 5 ml of deionized water was injected into the system. The polymerization was carried out under nitrogen at a constant stirring speed (400 rpm) for 4 hours. The cationic polymeric

microparticles were centrifuged twice under 60,000 rpm (Beckman L-80 ultracentrifuge) for 120 minutes to remove cationic surfactant.

The anionic microparticles were prepared using a method similar to the cationic microparticle preparation except that an anionic emulsifier (SDS) and initiator (potassium persulphate, KPS) were used.

### **Physical property measurements**

**PCC retention measurement:** The first-pass retention of PCC was measured using a Dynamic Drainage Jar (DDJ) with a 200-mesh screen. After 500 ml of pulp (0.4% BSK) and 0.5 g of PCC were added into the DDJ, the suspension was agitated under an 800-rpm stirring rate for 45 seconds, then the required polymer solution was followed. The suspension was continually agitated for another 15 seconds, then 150 ml of first-pass white water were collected. The white water from the DDJ was adjusted to pH ~ 3 using HCl and stood for 10 minutes at room temperature, then ~1 ml ammonia solution was added into the solution bringing the pH up to ~9.5. The calcium concentration was analyzed by potential titration using EDTA salt as a titrate. The end point of the titration was measured using a voltmeter, which was equipped with a calcium-selective electrode (Fisher product) and a pH reference electrode (Fisher product).

**Zeta potential:** The electrophoretic mobility was measured using a Zetasizer 2c (Malvern) at a stationary position, and the zeta potential was calculated by computer using the Smoluchowsky equation. The zeta potential of pulp fines was assumed to be representative of fibers.

**Particle size:** The particle size of cationic polymeric microparticles was determined by Doppler Electrophoretic Light Scattering using a Zetasizer 2c (Malvern).

**Colloid titration:** The charge densities of the cationic polymeric microparticle and cationic PAM were determined by colloid titration. One drop of orthotruidineblue indicator solution and 15 ml of 0.0001 N polyDADMAC were added into a 20-ml sample. The suspension was titrated to the colorimetric end point with 0.0001 N polyvinylpotassiumsulfate solution. The charge density of CPMP obtained by colloid titration is an apparent potential because the cationic repeat units in the polymer core may not be titrated by added polymers.

## RESULTS AND DISCUSSION

### Polymeric microparticle preparation

**Table 2** summarizes the preparation conditions and characteristics of the CPMPs used in this study.

Sample	A	B	C	D	E
Styrene (mmol)	108	108	108	108	108
Cationic surfactant (mmol)	0	3	2.2	8.2	0
Anionic surfactant (mmol)	0	0	0	0	10
Divinylbenzene (mmol)	4.3	4.3	0	4.3	4.3
Water (L)	0.15	0.15	0.15	0.15	0.15
VA-044 (mmol)	0.69	0.69	0.69	0.69	0
KPS (mmol)	0	0	0	0	0.69
Particle size (nm)	364	100	50	39	54
Zeta potential (mV)	40	54	-	56	-36
Charge density ( $\mu\text{eq/g}$ )	-	-	-	506	-

**Table 2.** Preparation of cationic polymeric microparticles.

The conversion of polymer D was 87% after a 4-hour reaction at 60 °C. It can be seen that the particle size of CPMP varies from 39 to 364 nm. The zeta potentials are -36 mV for anionic microparticles and +40 to +56 mV for cationic microparticles. It was found that the surfactant concentration is the most important factor affecting the particle size and surface charge.

### Retention of PCC using CPMP single retention aid

The flocculation of PCC caused by CPMP alone was reported in our previous publications [13]. The main conclusions from this early study are 1) the

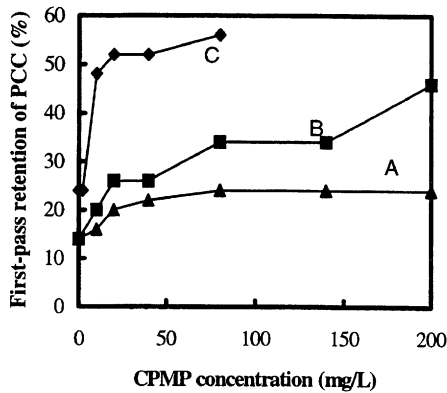
suspension of PCC dispersed in water cannot be flocculated by CPMP alone because both of them are positively charged; 2) the suspension of PCC dispersed in a  $\text{Na}_2\text{CO}_3$  solution can be flocculated by CPMP because the surfaces of PCC in this solution are negatively charged; 3) the addition of an water-soluble anionic polymer can further improve the flocculation of PCC by bridging formation between the negatively charged polymer and CPMP; and 4) the bridging formation between CPMP and the water-soluble anionic polymer depends on the sequence of the chemical addition.

It is well recognized that wet-end chemistry in paper manufacturing is a dynamic process, which never reaches an equilibrium. The flocculation results obtained in a static condition may not be used in a dynamic condition. Therefore, a dynamic drainage jar was used to measure the first-pass retention of PCC and simulate the dynamic condition of a paper machine in this study.

As shown in **Figure 1**, the improvement of PCC first-pass retention by CPMP depends on the properties of PCC and fibers. For PCC dispersed in a washed pulp, the first-pass retention of PCC increased little as the concentration of CPMP was increased. This is not surprising because the PCC in the washed pulp (free of anionic trash) is positively charged and there is no strong attraction force between positively charged PCC and positively charged CPMP [13]. However, the first-pass retention was improved when the PCC was dispersed in an original BSK pulp. The improvement of PCC retention in this system was due to the adsorption of anionic trash onto the PCC surface, which resulted in an increase in the attraction force between negatively charged PCC particles and positively charged CPMP. This was confirmed using an APAM-pretreated PCC in a washed pulp (see **Figure 1**).

It can be seen that the pretreatment of PCC by APAM can significantly improve the retention when CPMP was used as a retention aid. It is believed that, for the system of APAM-pretreated PCC in a washed pulp, the CPMP bridges formed through the patches of adsorbed APAM. Obviously, the bridging formation will strongly enhance the flocculation and retention of PCC. It should be noted that all of the retention results obtained at a dynamic condition were consistent with our previous study at a static condition [13]. From zeta potential and flocculation measurements, it was found that the most effective retention was obtained at the isoelectric point. It should also be noted that, although the retention of PCC in a BSK pulp can be enhanced by CPMP alone, it is less effective than the retention aids commercially used in papermaking.





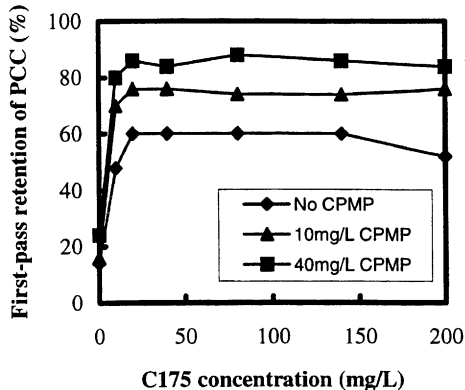
**Figure 1.** The first-pass retention of PCC on fiber web as a function of CPMP concentration. A: PCC in the washed BSK pulp; B: PCC in the original BSK pulp; and C: APAM-pretreated PCC in the washed BSK pulp.

#### Retention of PCC by dual retention systems of CPMP and a water-soluble polymer

It was indicated in our previous study that a water-soluble anionic polymer could enhance the flocculation ability of CPMP. In this study, the PCC retention induced by the dual systems of CPMP/polyelectrolyte was further studied at dynamic condition. The polymers were also extended to both anionic and cationic polyelectrolytes.

**Figure 2** shows that the combination of two cationic substances, CPMP and C175, can significantly enhance the retention of PCC. It has been seen from **Figure 1** that the maximum first-pass retention of PCC obtained by any single retention system (CPMP or C175) is less than 60%. However, as shown in **Figure 2**, the PCC retention could be greater than 80% if C175 was combined with CPMP. The dramatic increase in PCC retention using a combination of CPMP and C175 is surprising because both of them are positively charged. Obviously, this phenomenon cannot be explained by a simple model of polymer bridging. It is also believed that the increase in PCC retention by the combination of two cationic

substances is not simply a result of the charge neutralization because the experiment results showed a negative effect on the PCC retention if a polyDADMAC was used to neutralize the charges of fibers and fillers (see **Figure 3**).

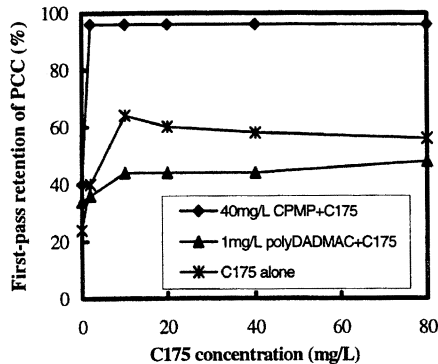


**Figure 2:** The effect of CPMP concentration on the first-pass retention of PCC in an unwashed BSK pulp.

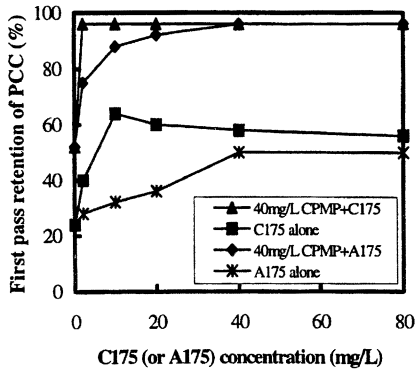
The PCC retention obtained by a CPAM-CPMP dual system was compared with that obtained by a CPAM-polyDADMAC dual system, and the results are shown in **Figure 3**. It should be noted that, for the same dual retention aids (40 mg/L CPMP + C175), different retention values were obtained in **Figure 2** and **Figure 3**. The reason for this is that different pulps and fillers were used in these two tests. For the test shown in **Figure 3**, the zeta potential of furnishes was first adjusted to zero by addition of polyDADMAC or CPMP before C175 addition. It can be seen that the prior addition of polyDADMAC slightly deteriorated rather than enhanced the PCC retention. In contrast to polyDADMAC, the prior addition of CPMP improved PCC retention significantly. The opposite results obtained by preaddition of polyDADMAC and CPMP suggest that the charge neutralization is not the dominant factor for flotation enhancement in this dual retention system.

**Figure 4** shows the results obtained by two types of dual retention systems, CPMP-C175 and CPMP-A175; the former contains two cationic, and the latter contains a cationic and an anionic component. It can be seen that both of the dual retention systems can lead to a 96% first-pass retention of PCC, although they have different charge characters. However, the dual retention system of CPMP-C175 is more effective compared to the system of CPMP-A175. Because the polymers of C175 and A175 have the same molecular weight but different charges (see **Table 1**), it may suggest that the combination of CPMP with a positively charged polymer is more effective than that with a negatively charged polymer. However, further study is needed for a general conclusion because the system is very complicated.

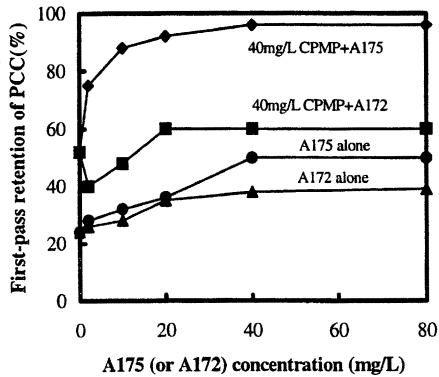
The retention efficiency of CPMP enhanced by anionic polymer addition is consistent with our previous flocculation study at a static condition [13]. It is believed that the improvement of the PCC retention using the CPMP-A175 dual retention aid is because of the bridging formation between CPMP and adsorbed anionic polymers. This mechanism has been proposed and discussed in our previous study. However, the retention induced by a dual retention system containing two cationic substances, CPMP and C175, has not been reported before, and the mechanism of this system will be discussed later.



**Figure 3.** The first-pass retention of PCC induced by preaddition of CPMP or polyDADMAC. The anionic charge demand of 40 mg/L CPMP is the same as 1 mg/L polyDADMAC. The washed pulp and APAM-pretreated PCC were used.



**Figure 4.** The first-pass retention of PCC induced by very high molecular weight polymers (cationic C175 and anionic A175) in the presence and absence of cationic polymeric microparticles. The washed BSK pulp and APAM-pretreated PCC were used.



**Figure 5.** The effect of CPMP on the performance of two different anionic retention aids, A175 and A172. The washed BSK pulp and APAM-pretreated PCC were used.

**Figure 5** shows the results of PCC retention induced by two anionic polymers, A172 and A175, in the presence of 40 mg/L CPMP. It can be seen that the first-pass retention of PCC obtained by CPMP-A175 is much higher than that obtained by CPMP-A172, although both A175 and A172 are negatively charged. Because there may be many differences between these two polymers, such as molecular weight, charge density, chemical structure, and polymer conformation, the reasons for the significant difference in retention are not clear. However, one of the major factors resulting in the different retention may be the difference in molecular weight. Because A175 has a very high molecular weight, but A172 has only a medium high molecular weight, the former may result in a more effective bridge.

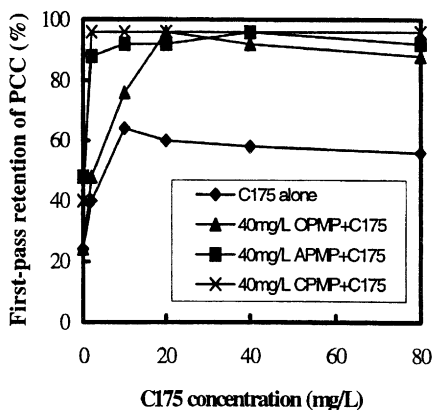
The finding in the present study suggests that, potentially, the combination of a cationic microparticle with an anionic polymer can be an effective retention system for papermaking, although it has opposite charge characteristics of commercially used microparticle retention aids. The general mechanism for an anionic microparticle retention system is that cationic polymer patches were first formed on the suspension surface; then the bridges were formed by following added anionic microparticles. In contrast, for the system of CPMP-APAM, the patches were first formed by adsorbed cationic microparticles; then the bridges were formed by an anionic water-soluble polymer.

#### **Polymeric microparticle charge effect on the PCC retention**

**Figure 6** illustrates the charge effect of a polymeric microparticle on the first-pass retention of PCC using cationic polymer C175 as a retention aid. Three types of microparticles were used: a cationic polymeric microparticle with a zeta potential of +56 mV and a particle size of 39 nm (sample D), a neutrally charged polymeric microparticle (OPMP) obtained by neutralization of sample D to a zero zeta potential using a low-molecular weight poly(acrylic acid), and a negatively charged polymeric microparticle with a zeta potential of -36 mV and a particle size of 54 nm (sample E). Additive order was polymeric microparticle first followed by cationic PAM.

It can be seen that all of the three types of the polymeric microparticles can significantly improve the first-pass retention of PCC, regardless of the original surface charge of the polymeric microparticles. It is interesting to note that the most effective dual retention system was the combination of two cationic substances, CPMP and C175. It should also be noted that the anionic microparticle in a high cationic PAM solution may no longer be "anionic" or at

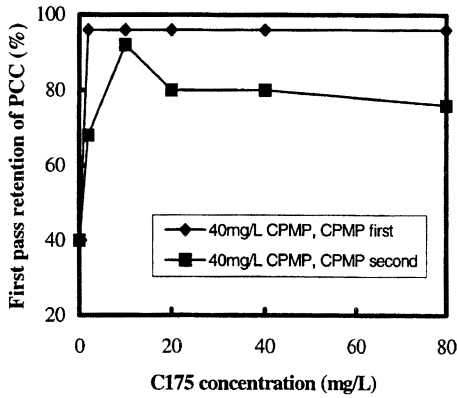
least partially cationic, because of the adsorption of CPAM on its surfaces. The adsorption of CPAM may also lead to a significant increase in the zeta potential of “zero charged” microparticles. This suggests that, at high concentrations of cationic PAM, all of the three microparticles may be considered as cationic rather than anionic or neutral microparticles. In other words, the results shown in **Figure 6** may not directly relate to the original charges of the microparticles. This complicity will be examined in our future study.



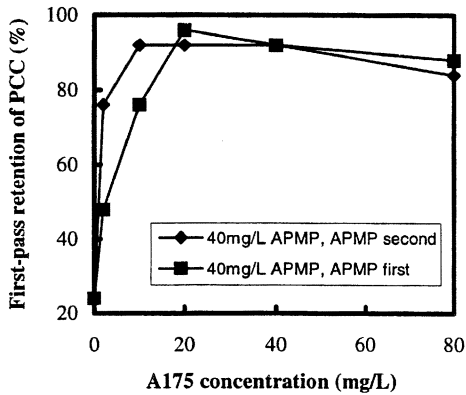
**Figure 6.** The effect of microparticle surface charge on the first-pass retention of PCC. A very high molecular weight and medium cationically charged polyacrylamide (C175) was used as a coflocculant. The washed BSK and APAM-modified PCC were used. The addition order was polymeric microparticle first and C175 second.

#### Additive order effect on the PCC retention

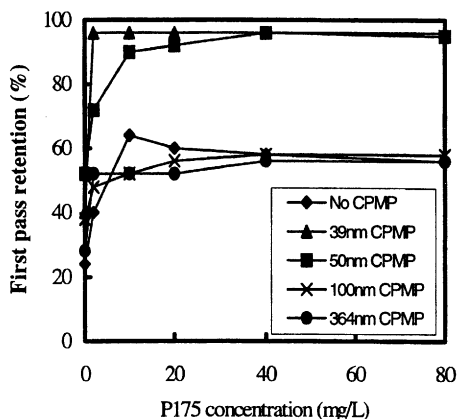
Because papermaking is a nonequilibrium process, the chemical additive order may significantly affect the retention efficiency. **Figures 7** and **8** show the results of first-pass retention of PCC obtained by different addition orders. For the dual retention system CPMP-C175, a higher retention was obtained when CPMP was added first. It is believed that, in the case of cationic C175 being added first, the adsorption of CPMP on the surfaces of fibers and fillers was resisted by the prior



**Figure 7.** The effect of polymer addition sequence on the PCC retention using a CPMP-C175 dual retention system.



**Figure 8.** The effect of polymer addition sequence on the PCC retention using an APMP-A175 dual retention system.



**Figure 9.** The effect of cationic polymeric microparticle size on the PCC retention when C175 was used as a cofloculant. The washed BSK pulp and APAM-pretreated PCC were used. The addition order was CPMP first and C175 second.

adsorbed CPMP. Obviously, the poor adsorption of cationic polymeric microparticles on fiber and filler surfaces results in a poor retention.

The dual retention system of C175 and APMP (anionic polymeric microparticle) is similar to the conventional anionic microparticle retention system used in the papermaking industry, such as colloidal silica and bentonite plus a cationic polymer. However, the mechanism of these microparticle systems has not been fully understood. We believe that the different addition sequences will result in different mechanisms. It can be seen from **Figure 8** that, at low polymer concentration, adding C175 first seems to be more effective than that of adding APMP first even though the difference is not significant. Improved retention in this system is probably due to the formation of anionic polymeric microparticle bridges as proposed in conventional microparticle systems [1]. Combining the results shown in **Figures 7 and 8**, it can be seen that the most effective retention system is CPMP-C175, and the addition order is adding CPMP first and C175 second.



### Particle size effect on the PCC retention

**Figure 9** shows the effect of CPMP particle size on the first-pass retention of PCC. As shown in **Table 2**, the surface charge of these particles is very similar. In this experiment, 40 mg/L CPMP were added before the addition of a positively charged, water-soluble CPAM. It is clearly shown that only the particles that have a size less than 50 nm improved PCC first-pass retention significantly, and the particles with a size larger than 100 nm did not have any positive effect on the retention

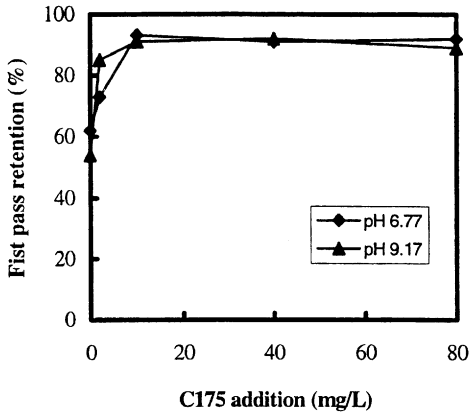
### Surfactant effect on the PCC retention

Because the microparticles used in this study were prepared in the presence of cationic surfactant, the surfactant effect on the first-pass retention of PCC was examined and the results are shown in **Figure 9**. The microparticles with particle sizes of 50 and 100 nm that contain 7% cationic surfactant (based on total solid weight) were used directly after the polymerization. However, the microparticles with 39 and 364 nm were a surfactant-free system that were purified by ultracentrifugation after polymerization. It can be seen that, in spite of the presence of surfactant in a 50-nm CPMP, the PCC retention was improved similar to that of a surfactant-free microparticle system (39 nm). This result may suggest that the surfactant remaining in CPMP does not significantly affect the retention of PCC.

### pH effect on the retention

Because the CPMP is positively charged at a pH up to 11 [13], it is expected that the CPMP can be used as a retention aid in both acid and alkaline conditions. This was tested using titanium dioxide as filler instead of PCC because of the high solubility of the latter at a low pH. In order to keep a high anionicity of TiO<sub>2</sub> surface at acid condition, an APAM-pretreated titanium oxide was used in this study. The primary results of total fine retention obtained by a CPMP-CPAM dual retention system are shown in **Figure 10**. Because only two pHs were tested, more work is obviously needed. However, the total fine retentions obtained at pHs 6.77 and 9.17 are almost identical. This is expected because APAM-pretreated TiO<sub>2</sub> is negatively charged and CPMP is positively charged at these conditions. It should be noted that even though the titanium dioxide has a much smaller particle size

than PCC, total fine retention can still reach 90% when the concentration of C175 reaches 8 mg/L.



**Figure 10.** The pH effect on the retention induced by a CPMP-C175 dual retention system. The washed pulp and APAM-pretreated  $\text{TiO}_2$  were used.

## DISCUSSIONS

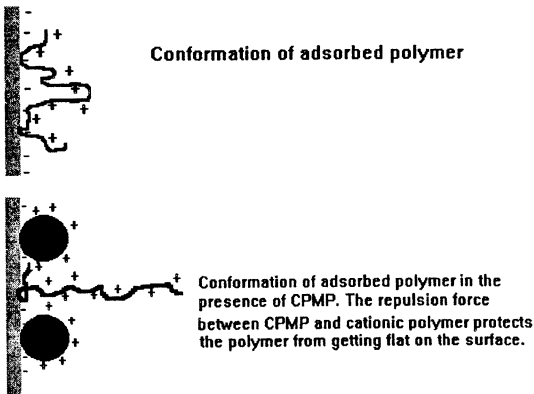
### The mechanism of retention using two cationic substances

It has been shown from the above discussions that the combination of CPMP with a high-molecular weight cationic polyacrylamide can significantly improve the flocculation or retention of fillers and fines, but the combination CPMP and cationic polyDADMAC reduced the retention of PCC fillers. This strongly suggests that the cationic microparticle behaves differently from common cationic coagulants.

It has been reported [21] that preaddition of cationic coagulants, such as polyDADMAC, decreases the adsorption amount of high-molecular weight CPAM on negatively charged suspensions because of the site-blocking effect. However, the prior adsorption of CPMP may not significantly affect the adsorption of high-

molecular weight CPAM because a larger uncovered surface area on the PCC surface was observed compared to polyDADMAC [13]. For example, the saturated adsorption amount of CPMP on the PCC surface was found to be as high as 18 mg/g, but the maximum surface coverage of CPMP on PCC was only 16%, which was much lower than the surface coverage by a water-soluble cationic polymer at the same adsorption amount. In other words, the prior adsorption of CPMP on a solid suspension will leave a large uncovered surface for further adsorption of a water-soluble cationic polymer, but the adsorption of a water-soluble cationic coagulant, such as polyDADMAC, will “block” the adsorption of the following added polymer.

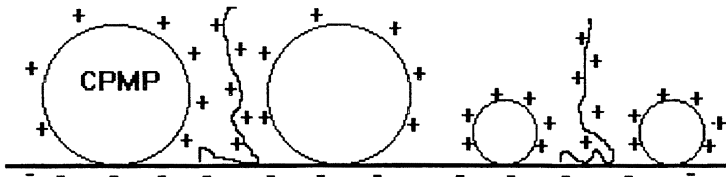
Another important factor that affects the filler and fine retention is the conformation of retention aids on the surface of suspensions. **Figure 11** illustrates the conformation of cationic polyacrylamide on a solid surface in the absence and presence of CPMP. Generally speaking, the flocculation efficiency is dominated by the length of adsorbed polymer if other parameters remain the same. Therefore, in the absence of CPMP, a high charge density cationic polymer will get flat on a negatively charged surface. However, in the presence of CPMP, the repulsion force between CPMP and cationic polymer will prevent the polymer from getting flat on the substrate surface. As a result, the polymer extrudes into liquid resulting in a longer bridge and a higher flocculation or retention.



**Figure 11.** Proposed conformation of cationic PAM at a negatively charged solid surface in the presence and absence of CPMP.

### The microparticle size effect on the retention

It has been seen from **Figure 9** that the first-pass PCC retention obtained by C175 was significantly improved by a CPMP, which has a particle size less than 100 nm, but was not enhanced if particle size of CPMP is larger than 100 nm. It has been known that the average radius of gyration for a cationic PAM with a molecular weight of 14 million is 300 nm. According to the mechanism suggested in this study (see **Figure 11**), the ratio of polymer chain length to particle diameter is a dominating factor for a retention induced CPAM-CPMP dual system. This can be clearly seen from **Figure 12**. If the polymer chain length is much longer than the CPMP diameter, the polymer may bond to another solid surface leading to a flocculation or retention. In contrast, if the polymer chain length is less than the diameter of CPMP, it is impossible to form polymer bridge between two suspended solid particles.



**Figure 12.** The effect of cationic microparticle size on the flocculation and retention using a CPMP-CPAM dual retention system.

### CONCLUSIONS

- (1) CPMP alone can improve the PCC retention, but the improvement is not significant, and it strongly depends on the anionic trash in the furnish.
- (2) The combination of a cationic polymeric microparticle with either a cationic or an anionic water-soluble polymer can significantly improve the PCC retention.

(3) The additive order of CPMP and CPAM will affect the PCC retention efficiency. For the PCC retention, the preaddition of CPMP is more effective than the preaddition of CPAM.

(4) The retention efficiency is cationic microparticle size dependent. The cationic microparticles with a size less than 100 nm will significantly improve the retention, but larger cationic particles do not enhance the PCC retention.

(5) Prior addition of a conventional high-charge density, low-molecular weight polymer to CPAM decreases the PCC retention, but the prior addition of a cationic microparticle increases the PCC retention.

(6) The surfactant present in the cationic microparticle system does not significantly deteriorate the PCC retention.

(7) pH does not significantly affect the CPMP performance in the range of 6.77 to 9.17.

(8) Effective patch formation of CPMP is considered to be the primary mechanism of PCC retention in the dual retention systems studied. The CPMP patches may affect the conformation of a soluble cationic polymer on fiber and filler surfaces.

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# Transcription of Discussion

## **Cationic microparticle retention aids: the mechanism - study and laboratory evaluation**

*Yulin Deng, Associate Professor, IPST, USA*

*Professor Tom Lindström, Royal Institute of Technology (KTH), Sweden*

Do your micro particles share the features of the commercial anionic micro particles such as bentonites and silicas. We try to classify them because they share features such as forming condensed flocs and reversibility of flocculation. Do your cationic micro particles share the same features?

*Yulin Deng*

No I don't think that's the same feature. We think that the co-bridging formation between the micro particle and the polymer is accepted as true by most people, but in this case (cationic microparticle plus cationic polymer) I believe that the configuration change is the dominating mechanism here.

*Kevin Hodgson, Associate Professor, University of Washington, USA*

I'm curious about your sizing results with your cationic particles. Were these samples treated in exactly the same way?

*Yulin Deng*

Yes in exactly the same way we treated them with and without cationic polymer. These results were without any other polymer addition, we only used micro particles. We made the handsheets after heating to 110°C.

*Kevin Hodgson*

Can you speculate as to why there seems to be such a massive change in the water holdout of the paper? Was it 0.2 and 0.4 and did you explore that region any further in terms of seeing what happens in between there?



*Yulin Deng*

We did. We have more data on the sizing. What we found was that we didn't see the transition between low concentration, say 0.4 to 0.8. We still do not see a sharp sizing efficiency increase because we have not studied in detail about the adsorption of polystyrene microparticles on the fiber surface so I cannot answer that.

*Dr Theo van de Ven, Director, Paprican/McGill, Canada*

Did you verify whether or not cationic polyacrylamide adsorbed on your micro particulate particle, for example, it's well known that cationic polyacrylamides adsorb on calcium carbonate particles.

*Yulin Deng*

We haven't done this adsorption measurement. What we see is that without cationic micro particles, only cationic polymer, the retention is poorer than the mixture but we don't know how the interaction happens.

*Theo van de Ven*

Does your cationic polyelectrolyte flocculate your micro particulate system?

*Yulin Deng*

This is a dilute system - only 2-3 ppm of micro particles. We cannot see the flocculation.

*Theo van de Ven*

Then I have a suggestion as to what you might do in order to test your model. If you first cover your surface with a known amount of micro particulate systems and then you do adsorption experiments with your polymer, if your model is correct, there should be strong correlation between the available spaces between the particles and the adsorbed polyacrylamides.

*Dr Kari Ebeling, Director, UPM Kymmene Group, Finland*

Have you studied what happens in recycling if you heat cure your micro particulates and try to re-make paper after recycling. Is the bonding as easy as it is with a normal fibre?

*Yulin Deng*

We haven't measured paper physical properties using recycled fibre. We have done some work on OCC to study the retention of PCC using our cationic microparticles. We found that the PCC retention can be improved by adding cationic micro particle. We don't know the final paper properties.

*Ian Thorn, European Business Development Manager, EKA Chemicals Ltd, UK*

A comment on your first slide - we have been running in a papermill which is just about 100% closed without seeing any silica deposits.

Secondly, did you measure the cationic demand of your stock after you have added PCC, cationic microparticle and the cationic polyacrylamide?

*Yulin Deng*

We didn't measure the total cationic demand but we measured the zeta potential of the fines and fillers in order to follow positive or negative charges. We don't know the total demand.

*Lars Wågberg, Research Manager, SCA Research AB, Sweden*

You state that if you absorb first POLYDADMAC and then CPAM and compare that to adding first the cationic micro particle and then the CPAM, the cationic micro particle leaves a larger uncovered surface. How have you compared that? Is it on a charged basis so that you add the same charge with the cationic micro particle or is it calculated on coverage from a geometrical point of view?

*Yulin Deng*

We've calculated uncovered surface area by cationic micro particles which gives poor cover, only 38% of the area I believe. There are a lot of uncovered spaces. In this

experiment we only added the same amount based on the charge, not based on the surface coverage so it's the same amount of cationic total charge not surface area

*Lars Wågberg*

I was a bit surprised because the POLYDADMAC can be assumed to reconform on the surface to lie flat whereas your cationic micro particle is supposed to keep its dimensions so they would obstruct the adsorption of further CPAM even more.

*Yulin Deng*

This is the assumption for that mechanism. Recently we have had some professors who will work on computer modelling to see if this is a possible configuration. We will also measure the adsorption of the surface layer. More work is needed to give conclusions about the mechanism.