

Cationic microparticle based flocculation and retention systems

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Abstract

Two types of microparticles, cationic silica particles (CSP) and cationic polymeric microparticles (CPMP), were used as flocculants and retention aids for solid suspensions in water and pulp, respectively. The solid suspensions used in this study include both positively and negatively charged precipitated calcium carbonate (PCC) and negatively charged polystyrene latex. It was found that CPMP was not an effective retention aid for positively charged PCC suspension in pulp if it was used alone. However, the retention of PCC was improved when negatively charged PCC was used. The combination of cationic microparticle systems (CPMP and CSP) with either cationically or anionically charged water-soluble polyacrylamides could significantly improve the flocculation and retention. The possible mechanisms of flocculation of solid suspensions with different dual-flocculant systems were discussed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the past two decades, many new flocculation systems that are superior to traditional linear polymers have been developed. One of the innovations in the paper industry is the use of microparticle flocculation systems to improve the retention and drainage during papermaking [1]. In this system, the flocculation is induced by the sequential addition of a positively charged polymer followed by negatively charged microparticles, such as bentonite and colloidal silica [2–6]. A widely accepted flocculation mechanism is that cationic patches are first formed on the negatively charged fibers, fines and fillers, then the anionic microparticles form bridges between suspended particles and fibers through pre-adsorbed cationic patches.

Currently, all commercial microparticle systems are based on anionic microparticles. The use of cationic latex and inorganic microparticles as paper additives and retention aids has only been reported in literatures. Alinec and co-workers [7–9] have studied the interaction of cationic latex and mineral fillers with wood fibers, and suggested that the deposition of clay, TiO₂, and latex proceed in full agreement with the theoretical predication of heterocoagulation of oppositely charged particles. Rushmere [10] claimed the dual system of cationic silica and anionic polyacrylamide is an effective retention aid. Svending [11] described another dual retention system based on cationic silica and cationic polymer. Our previous study [12] indicated that pre-added

CPMP could improve anionic polyacrylamide's flocculation efficiency. Recently, Ovenden et al. [13] reported that the flocculation and retention of fillers could be significantly improved by using colloidal alumina microparticles with an anionic polyacrylamide.

Although the past works indicated cationic microparticles with water-soluble polymers could be effective retention aids for papermaking, the fundamentals of these systems have not been well studied. In this study, the flocculation and retention of PCC in pulp with CPMP and cationic polymer were first investigated. Then the flocculation mechanism of cationic microparticle systems, including single and dual systems, was studied by using polystyrene latex as a model suspension.

2. Experimental

2.1. Materials

Cationic polymeric microparticle (CPMP) was prepared using emulsion polymerization and purified as described in the previous paper [12]. Negatively charged polystyrene latex (as a suspension) was prepared using emulsifier-free polymerization as described by Goodwin, et al. [14]. Cationic silica particle (Eka Nobel Chemicals) was an alum modified silica sol.

Precipitated calcium carbonate (Specialty Mineral) was a scalenohedral calcite product with an average size of 1.3 μm and specific surface area of 12 m²/g. Negatively charged PCC was prepared by the following method. A

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Table 1
Physical properties of the microparticles, polystyrene latex and polymers

Materials	Molecular weight ^a (g/mol)	Mean particle size (nm)	Charge density (meq/g)
CPMP	–	39	0.51 ^b
CSP	–	40	0.61 ^c
Polystyrene latex	–	480	–0.018 ^d
C175 (CPAM)	Very high	–	1.09
A172 (APAM)	High	–	–0.44

^aReported by manufacturer.

^bEqual to 33.7 $\mu\text{C}/\text{cm}^2$.

^cEqual to 78.4 $\mu\text{C}/\text{cm}^2$.

^dEqual to –14.6 $\mu\text{C}/\text{cm}^2$.

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 separated by centrifugation and washed two times with deionized water. The APAM-pretreated PCC showed a strong negative charge and formed relative stable dispersion in water. The cellulose fibers were once dried bleached softwood kraft pulp (BSK). Clean fibers were prepared by washing the pulp several times with deionized water and filtrated using a 200-mesh screen.

Cationic polyacrylamide (CPAM) Percol[®] 175 and anionic polyacrylamide (APAM) Percol[®] 172 (Allieds Colloid, abbreviated as C175 and A172, respectively) were used as water-soluble flocculants. The properties of these polymers are given in Table 1.

2.2. Physical property measurement

The mean size of the particles was determined by photon correlation spectroscopy at 25°C using a Malvern Zetasizer 3000 (10 mW 633 nm He–Ne laser) at a 90-degree angle. Zeta potential was measured using a Malvern Zetasizer 3000 at a stationary position. The surface charge was determined by colloidal titration using ortho–toluidine blue as indicator. The physical properties of the microparticles and polystyrene latex are also given in Table 1.

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 s, then the required polymer solution was followed. The suspension was continually agitated for another 15 s, then 100 ml of first-pass white water was collected. The white water from the DDJ was adjusted to pH \sim 3 using HCl and stood for 10 min at room temperature, then \sim 1 ml ammonia solution was added into the solution bringing the pH up to \sim 9.5. The calcium concentration was analyzed by potential titration using EDTA salt as 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).

The flocculation of polystyrene latex was conducted at pH 4.5 in water and was determined as follows. A quantity of 10 ml of 1 g/l polystyrene latex was added into a 50 ml tube. The required amount of cationic silica or polymer was added, and the final volume of the solution was adjusted to 20 ml with water. The mixture was immediately shaken for about 10 s, and then the flocculated mixture was allowed to stand for 1 h at room temperature. For the dual-flocculant system, the second flocculant was added 1 min after the first flocculant. Small amount of the sample (4 ml) was carefully pipetted from the top, and the transmittance was measured using a Shimadzu UV160U spectra photometer at 550 nm. Deionized water was used as reference (transmittance = 100%), and the polystyrene latex solution without adding any flocculant was used for the baseline measurement (i.e. the initial turbidity τ_0). The relative turbidity, τ/τ_0 was used to determine the flocculation ability, where τ and τ_0 are the turbidities of the suspensions with and without flocculant, respectively.

3. Results and discussion

The experiments covered several subjects that include the retention of PCC on wood fibers with CPMP and cationic polymers, and the flocculation of negatively charged polystyrene latex with CSP and polyacrylamides (both CPAM and APAM). The results are separately discussed as follows.

3.1. Retention of PCC

The retention of PCC in pulp with CPMP and cationic polymer was studied in a dynamic drainage jar. As shown in Fig. 1, the improvement of the 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 is positively charged and there is no strong attraction force between positively charged PCC and positively charged CPMP [12]. However, the first-pass retention was improved when the PCC was dispersed in an original

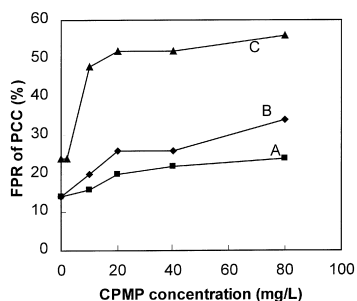


Fig. 1. The first-pass retention of PCC in wood pulp as a function of CPMP concentration. (A) PCC in the washed BSK pulp; (B) PCC in the original BSK pulp; (C) APAM-pretreated PCC in the washed BSK pulp.

BSK pulp, which contain many anionic substances such as lignin, xylan, D-glucuronic acid- α -lactone and fiber fines. The improvement of PCC retention in this system was due to the adsorption of the anionic substances 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 by using an APAM-pretreated PCC in a washed pulp. 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 formed bridges through the patches of the pre-adsorbed APAM on the PCC surface. Obviously, the bridging formation will strongly enhance the flocculation and retention of PCC.

Fig. 2 shows that the combination of two cationic substances, CPMP and C175, can significantly enhance the retention of PCC. It can be seen that the maximum first-pass retention of PCC obtained by CPMP or C175 alone is <60%. However, the PCC retention was >95% when C175 was used in combination with CPMP. It has been reported [15] that pre-addition of cationic coagulants, such as poly-DADMAC, decreases the adsorption amount of high molecular weight CPAM on negatively charged suspensions while maintaining the flocculation efficiency because of site-blocking effect. Because CPMP is a rigid particle and it cannot spread on PCC surface during the adsorption,

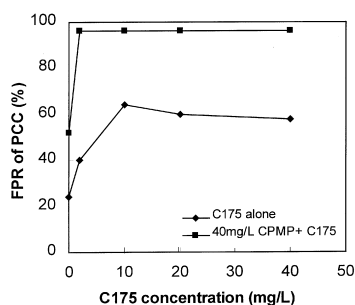


Fig. 2. The first-pass retention of PCC induced by C175 in the presence and absence of cationic polymeric microparticles. The washed BSK pulp and APAM-pretreated PCC were used.

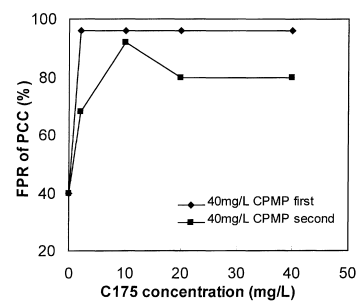


Fig. 3. The effect of polymer addition sequence on the PCC retention using a CPMP-C175 dual retention system.

the surface area of PCC occupied by adsorbed CPMP has been found to be very small [12]. This suggests that site-blocking effect for the CPMP system is less important than a highly charged cationic water-soluble polymer, such as poly-DADMAC. In addition, the significant increase of the retention efficiency also cannot be explained simply by site-blocking effect. One possible reason for the enhancement of PCC retention by the combination of CPMP and C175 is that the pre-adsorbed CPMP may affect the conformation of cationic polymer on the PCC surface by the electrostatic repulsion force between these two substances.

Fig. 3 shows the results of the first-pass retention of PCC obtained by CPMP-CPAM dual system with different addition orders. A higher retention was obtained when CPMP was added first. It is believed that different addition orders could lead to different adsorption amount and the conformation of C175 on PCC and fiber surfaces, therefore, resulting in different flocculation results.

3.2. Flocculation of negatively charged polystyrene latex by dual-flocculant system of cationic particle and cationic polymer

It has already been found that using the dual flocculation system of cationic microparticle and a cationic polymer could significantly enhance the retention of PCC in wood pulp. This dual-flocculant system is very interesting since it is different from a traditional dual-flocculant system in which two oppositely charged flocculants are usually involved. In order to study the mechanism of this cationic dual-flocculant system, the flocculation of negatively charged polystyrene latex suspension by cationic silica particle and C175 was studied.

Fig. 4 and Fig. 5 show the effect of single flocculant on the zeta potential and relative turbidity of the latex suspension. The added amount of flocculant (mg/g) is based on the total amount of polystyrene latex. It was found that the maximum flocculation of latex with C175 was obtained near to the isoelectric point (IEP). A further increase in the concentration of cationic flocculant (C175) resulted in an increase in the relative turbidity, which indicated the latexes were re-stabilized. The maximum flocculation at IEP

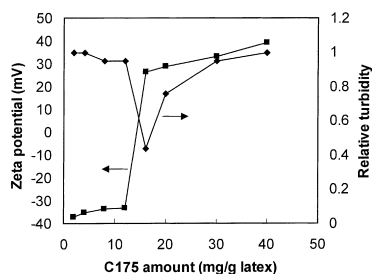


Fig. 4. Relative turbidity and zeta potential of polystyrene latex as a function of C175 concentration.

is commonly considered as an indication of neutralization coagulation rather than bridging flocculation. Although it is normally considered that the flocculation of solid suspensions caused by a high-molecular weight and low-charge density polyacrylamide is through the bridging formation mechanism [16–18], the results here may indicate that an effective bridging will also be affected by the surface charge of the solid suspension, i.e. the higher the surface charge, the more difficult to form an effective bridging. Because the charge density of the polystyrene latex used in this study is high ($14.6 \mu\text{C}/\text{cm}^2$), the most effective bridging formation at IEP should not be surprised. Furthermore, because the turbidity and zeta potential measurements were conducted 1 h after the addition of the flocculant, the adsorbed cationic polymers should have enough time to rearrange their conformation on the polystyrene latex surface, which may result in a transition from bridging to charge neutralization.

The flocculation of polystyrene by CSP is different from that by C175. It can be seen from Fig. 5 that the maximum flocculation of the latex by CSP alone occurred when the zeta potential of the latex was still very negative. The results indicate the CSP caused flocculation mainly through microparticle bridging. Because CSPs are rigid particles, the conformation of CSP will not change during flocculation. This means that the bridging formation can be the only mechanism for this special system. The increase in the relative turbidity at high CSP concentration indicates that the polystyrene latexes could also be re-stabilized by adsorbed cationic particles.

Fig. 6 shows the flocculation results from a dual CSP-CPAM flocculation system with the pre-addition of 10

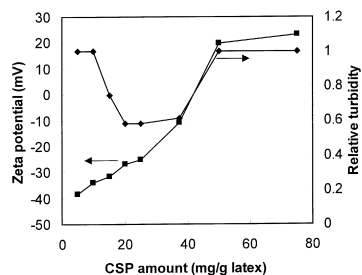


Fig. 5. Relative turbidity and zeta potential of polystyrene latex as a function of CSP concentration.

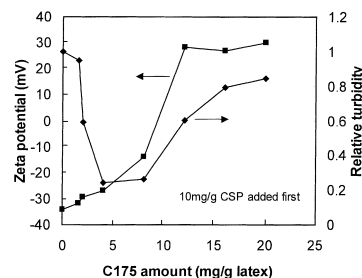


Fig. 6. Relative turbidity and zeta potential of polystyrene latex as a function of C175 concentration in the presence of pre-added CSP.

mg/g CSP. It should be noted that almost no flocculation was observed if 10 mg/g CSP was used alone (Fig. 2). It can be seen that an effective flocculation occurred when a dual CSP-CPAM flocculation system was used. It was also noted that maximum flocculation occurred when the zeta potential was still negative, and the concentration of C175 for the effective flocculation shifted to a much lower concentration range in this dual-flocculant system than in a single C175 system. The results clearly indicated that the flocculation was through bridging formation rather than charge neutralization. It is generally known that the flocculation efficiency will be dominated by the conformation of the adsorbed polymer on a substrate surface if other parameters remain the same. In the absence of CSP, the cationic water-soluble polymer may get flat on the latex surface, and therefore the length of polymer loops is short. However, in the presence of CSP, the repulsion force between CSP and C175 will prevent C175 from getting flat on the latex surface. As a result, C175 extrudes into liquid to form more effective bridges, and thus gives a better flocculation.

From the above discussion it is obvious that the pre-addition of CSP is important because it will affect both the conformation and the adsorption amount of cationic water-soluble polymer. If the above assumption is correct, the addition order of the CSP and C175 should significantly affect the flocculation efficiency. Fig. 7 shows the flocculation results obtained by the same dual cationic flocculant system but in different addition orders. It can be seen that when water-soluble cationic C175 was added first, not only was the maximum flocculation efficiency reduced, but the

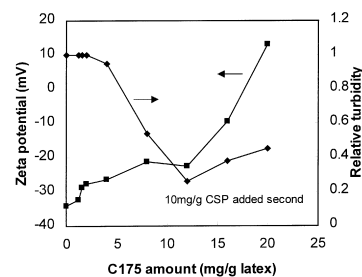


Fig. 7. Relative turbidity and zeta potential of polystyrene latex as a function of C175 concentration in the presence of CSP. CSP was added after C175.

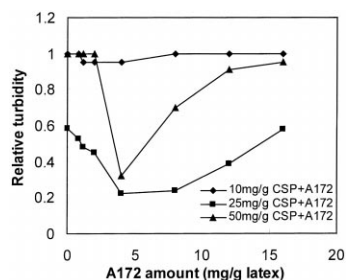


Fig. 8. Relative turbidity of polystyrene latex as a function of A172 concentration at different pre-added amounts of CSP.

amount of cationic polymer C175 needed to reach the maximum flocculation was also significantly increased. The level rivaled that of C175 alone. When C175 was added first, the addition of CSP should not significantly affect the adsorption amount and conformation of C175. As a result, the flocculation of suspension by adding C175 first followed by CSP should not significantly differ from that of using C175 alone.

3.3. Flocculation of polystyrene latex by dual-flocculant system of cationic particle and anionic polymer

Our previous study on the flocculation of precipitated calcium carbonate (PCC) indicated that the combination of cationic polymeric microparticles with anionic polyacrylamide could significantly improve the flocculation efficiency [12]. The suggested flocculation mechanism is that the cationic polymeric microparticles first create effective patches on the PCC surface, then the anionic polyacrylamide forms interparticle bridges through those positively charged patches. This suggested mechanism was further investigated in this study using negatively charged polystyrene latex instead of PCC suspension, and cationic silica particles instead of cationic polymeric microparticles. Fig. 8 shows the effect of the flocculation system of CSP and negatively charged polymer A172 on the turbidity of the polystyrene latex. Corresponding zeta potentials of the polystyrene latex at the same conditions used in Fig. 8 are given in Fig. 9. At a dosage of 10 mg/g pre-added CSP, the addition of A172 could only lead to a very weak flocculation. However, when

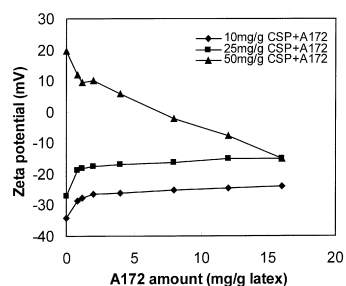


Fig. 9. Zeta potential of polystyrene latex at the same conditions used in Fig. 8.

the pre-added amount of CSP increased to 25 mg/g, the flocculation efficiency was significantly improved by adding negatively charged polymer A172. The increased flocculation efficiency could not be explained by the charge neutralization mechanism because the electrophoretic mobility of the latex was still negative at this point. The possible mechanism for this dual flocculation system is the bridging formation of A172 through the positively charged CSP patches on the latex surface. It is interesting to note that although A172 is negatively charged, the zeta potential of the latex turned out to be less negative by initial added A172 and then maintained almost constant with more A172. The reason for this phenomenon is not clear. When the pre-added amount of CSP reached 50 mg/g, A172 caused maximum flocculation at near IEP. The flocculation results are very similar to that of C175 alone (Fig. 4). This may indicate that the neutralization of the surface charge on the solid suspension can improve the polymer bridging efficiency when the charge density on the solid suspension is high.

4. Conclusions

Cationic polymeric microparticles alone can improve the PCC retention in wood pulp, but it strongly depends on the presence of anionic trash in the pulp. The combination of CPMP with a cationic polymer can significantly improve the PCC retention. For the flocculation of negatively charged polystyrene latex, both water-soluble cationic polymer and cationic silica particle are not very effective flocculants if they are used alone. However, the flocculation efficiency can be significantly improved if the cationic silica particle is used in combination with a cationic or anionic polymer. For the dual-flocculant system containing two cationic components (cationic silica particle and a cationic water-soluble polymer), the pre-adsorption of cationic silica particles may affect the conformation of the polymer on the latex surface. The charge repulsion between pre-adsorbed cationic silica particle and cationic water-soluble polymer may prevent the polymer from getting flat on the latex surface, thus the flocculation efficiency of cationic water-soluble polymer can be significantly improved. For the dual-flocculant system of a cationic particle and an anionic polymer, the cationic particle may first form cationic patches on the latex surface, and then the anionic polymer forms bridges through these patches. This conclusion agrees very well with our previous finding [12].

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