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Polystyrene and Polyacrylate-Based Cationic Copolymers and
Their Colloidal Dispersion—Novel Polymers for the Paper Industry

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POLYSTYRENE AND POLYACRYLATE-BASED CATIONIC COPOLYMERS AND THEIR COLLOIDAL DISPERSION—NOVEL POLYMERS FOR THE PAPER INDUSTRY

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ABSTRACT

Polystyrene or polyacrylate-based cationic copolymers contain both hydrophobic and hydrophilic components. The solubility and colloidal behavior of the copolymers in water strongly depends on the fraction of the cationic component in the copolymer backbone. By controlling the charge density, the copolymers can be water insoluble, colloidally dispersible, or fully water soluble. These unique properties have led to many potential applications in areas such as paper coating, paper sizing, and papermaking retention. Several methods, including emulsion polymerization, miniemulsion polymerization, and solution polymerization, have been studied for preparation of the cationic copolymers. It has been found that emulsion polymerization resulted in two different fractions, hydrophobic enriched and hydrophilic enriched fractions, in preparing high cationically charged copolymers. High cationically charged copolymer might be prepared by solution polymerization. Miniemulsion polymerization with a dual initiator system has also been used for preparing the copolymers. The copolymers were characterized and their colloidal properties in water are reported. The potential applications of these copolymers and colloidal dispersions in the papermaking, paper recycling, and pressure-sensitive adhesives industries are discussed.

Because most applications of cationic water-dispersible polymers strongly depend on the particle size, charge density, and uniformity, different methods of synthesizing the copolymers and colloidal particles were first reviewed for this paper. The applications of these colloidal particles in the paper industry, which include retention, sizing, and adhesives, are followed. It will be seen that both retention and sizing efficiency can be significantly improved by reducing the size of cationic colloidal particles.

INTRODUCTION

Copolymers containing both hydrophobic and hydrophilic units in the polymer backbone have attracted much research attention recently because of their potential applications as catalysts [1,2], papermaking aids [3-7], and coating agents [8]. These applications strongly depend on colloidal properties such as charge density, particle size, uniformity, etc. In some applications, such as papermaking aids, very small particle size and high cationic charges are needed. From our knowledge, there is no available method for preparing uniform, high charge density, and very small cationic colloidal particles. In our

previous studies, several polymerization techniques for preparing these unique colloidal particles have been studied [9-12], and the results are reviewed in this paper.

Polystyrene and polyacrylate-based cationic copolymers have unique properties when they are dissolved or dispersed in water. The hydrophilic-hydrophobic balance of the copolymer has a significant effect on its solubility and dispersibility in water. At very low charge density, the hydrophobic attractive force is the dominating force that causes a phase separation of the copolymer in water. When the cationic charge content increases, the van der Waal's forces between hydrophobic polystyrene or polyacrylate backbone promotes an aggregation, while the electrostatic repulsion forces between cationically charged monomers protect the aggregates from unlimited growth of the particles. As a result, stable colloids are formed. When the cationic fraction is further increased, the copolymer can be fully dissolved in water to give a true solution. The hydrophilic-hydrophobic balance in the copolymers affects not only the solubility of the copolymer in water but also the particle size and surface charge of the colloidal dispersion. Our study showed that cationic polystyrene colloidal particles with particle size from 30 to 200 nm could be prepared. These very small colloidal particles have many potential applications, which will be discussed in this article.

Synthesis, Characterization, and Colloidal Properties of Cationic Polymers

Synthesis of copolymers containing both hydrophobic and cationic hydrophilic units has been studied in the literature. Emulsion polymerization techniques have been widely applied to synthesize cationic polymeric latexes. However, there are several problems in using emulsion polymerization techniques for preparation of this type of copolymer. First, because cationic monomers are strongly hydrophilic and are not miscible with the hydrophobic monomers in water, the incorporation rate of cationic monomers to the polymer through direct emulsion polymerization is low. Brouwer [13] studied the emulsion polymerization of styrene (80-100 wt%) and [2-methacryloxy)ethyl]trimethyl-ammonium chloride (MAETAC, 0-20 wt%), and found that the maximum incorporation of MAETAC to the latex was less than 4 wt%. Second, because the solubility of cationic monomers in water is significantly different from that of hydrophobic monomers, the emulsion copolymerization of these two different monomers usually results in two polymeric fractions, i.e., a high-cationic-monomer-containing copolymer and a high-hydrophobic-monomer-containing copolymer. Third, emulsion polymerization cannot be used to prepare a high-cationic-containing copolymer because the copolymer will be water soluble and it cannot exist in a latex form in water if the cationic content is high.

High charged cationic copolymers have been synthesized by cationization of the copolymers that contained functional monomers [2,11,14-17]. The problems of polymer modification are low efficiency, high cost, and nonuniformity. Cationic polymers have also been synthesized by solution polymerization in polar organic solvents [11,17-19]. Although the copolymers with high cationic content have already been synthesized for various applications, the details of the synthesis and the colloidal properties of this type of copolymer have not been well addressed. In our recent study [20] a series of copolymers of butyl acrylate (BA) and [3-(methacryloylamino)propyl]trimethyl-

ammonium chloride (MAPTAC) with different cationic content was synthesized by solution polymerization and characterized. The effect of reaction conditions on the properties of the copolymers was studied, and the reaction kinetics was reported. When solution polymerization is used to prepare a homogeneous poly(BA-*co*-MAPTAC), the choice of the right solvent is critical. First, both BA (hydrophobic) and MAPTAC (cationic and hydrophilic) should be soluble in the solvent used. Second, the solvent should also be a good solvent for the copolymer to prevent the precipitation of the copolymers. Third, both monomers should have reasonable monomer reactivity ratios in the solvent. Ethanol and methanol are strong polar organic solvents and were found to fit these requirements very well.

Cationic Polymers from Emulsion Polymerization

Emulsion polymerization was used to synthesize low charged cationic colloidal particles as reported in our previous study [9]. Styrene, MAPTAC, and divinylbenzene (DVB) were used as hydrophobic backbone, cationic comonomer, and crosslinker, respectively. 2,2'-azobis(N,N'-dimethyleneisobutyramidine) dihydro-chloride (VA-044) was used as initiator and cetyltrimethylammonium bromide was used as cationic surfactant. The properties of the colloidal particles prepared are given in Table 1.

Generally speaking, both the size and electrostatic properties of the colloidal particles prepared from emulsion polymerization are a function of the concentrations of surfactant, crosslinker, cationic monomer, and temperature. It can be seen that the surfactant concentration is the most important factor for controlling the particle size. An increase in the particle size with an increase in the cationic monomer content was also found, and this was attributed to the swelling of the colloidal particles if the charge density of the copolymer is high. It was also found that there were two fractions, high and low charge density fractions, in the final products prepared by emulsion polymerization. Furthermore, when high cationic monomer were added, the emulsion was not stable. Our study suggests that normal emulsion polymerization cannot be used for synthesis of high charge density and uniform copolymers.

Cationic Polymers from Miniemulsion Polymerization

Most recently, Gilbert [21] proposed that by selecting a dual initiator system such as cumene hydroperoxide/tetraethylpentamine (CHP/TEPA), it is possible to make extensive grafting of hydrophilic monomers onto a hydrophobic polymer by an emulsion process. In this dual initiator system, CHP is oil soluble and TEPA is water soluble. When they meet each other at oil/water interface, free radicals are produced. This unique property has been investigated and their application in synthesizing high cationically charged hydrophobic polymers has been studied [22]. Miniemulsion technique was used in the copolymerization of BA and MAETAC with CHP/TEPA as a dual initiator system. Triton X-405 was used as surfactant and hexadecane as co-surfactant. Two levels of cationic monomer MAETAC feed ratio, 3.1 mol% and 8.1 mol%, were used. It was found that in all cases, about 18% of MAETAC was homopolymerized in the water phase. The composition of the copolymer was very heterogeneous. With increased

conversion, the BA content decreased and MAETAC content increased. Further increasing the MAETAC feed ratio resulted in viscous and unstable emulsion products.

Cationic Polymer from Solution Polymerization

It is already known that emulsion polymerization cannot be used to prepare high cationically charged copolymers. Even at low cationic monomer content, high surfactant concentration has to be used in order to prepare very small cationic latexes (20-40 nm). Alternatively, solution polymerization using polar solvents in the absence of surfactant for cationic copolymer preparation was extensively studied. The resulting copolymers from solution polymerization can either form small colloidal particles in water or be water soluble depending on the charge density of the polymers.

One of our studies was to synthesize copolymers of styrene and vinylbenzyl trimethylammonium chloride (VBTMAC) in ethanol with VA-044 as initiator. The details of the solution polymerization for preparing small cationic colloidal particles in water were given in our early report [11]. The water solubility of the poly(styrene-co-VBTMAC)s is shown in Table 2. It can be seen that the solubility of the copolymers is affected by the cationic content and dispersing temperature. Stable colloidal particles with different sizes and charge density can be easily obtained. The formation of stable colloidal particles for certain poly(styrene-co-VBTMAC)s is not surprising because the van der Waal's forces between hydrophobic polystyrene backbones promote an aggregation, while the electrostatic repulsion forces between cationically charged VBTMACs protect the aggregates from unlimited growth. As a result, stable colloids were formed.

The temperatures indicated in Table 2 were those used for copolymer solution preparation. The particle sizes were measured at room temperature. It is interesting that although some samples could not be dissolved in water at room temperature, once they formed a colloidal dispersion at high temperature they remained as a colloidal stable dispersion even though the temperature was cooled down to room temperature. This phenomenon suggests that at low temperature, the copolymer chains entangled each other in solid state and high solvation energy is needed to dissolve the copolymer. However, when the temperature is increased the thermodynamic energy of polymer chains increases, resulting in an increase in the solubility of copolymers in water. When the thermodynamic energy, van der Waal's forces, and electrostatic repulsion forces are balanced, stable colloids are formed. However, when the temperature is cooled down, the electrostatic repulsion forces between colloidal particles provide a high energy barrier between the particles, which protects the coagulation of the colloidal particles. As a result, stable colloidal suspensions can be obtained through this temperature change cycle.

The main advantages of the copolymers from solution polymerization are: (1) no emulsifier is needed; (2) copolymers with different charge content can be easily obtained; (3) the colloidal particle size can be easily controlled by both the charge density and copolymer dispersing temperature.

In addition to studying copolymerization of styrene and VBTMAC, copolymerization of BA and MAPTAC in ethanol and methanol was also investigated [20]. The copolymerization of BA (M_1) with MAPTAC (M_2) gave reactivity ratios as $r_1 = 0.92$ and $r_2 = 2.61$ in ethanol, and as $r_1 = 0.79$ and $r_2 = 0.90$ in methanol. Studies indicated that random copolymers could be prepared, and the molar fractions of BA and MAPTAC were close to the feed ratios. With increased cationic content, the water solubility/dispersibility of the copolymer increased.

Applications of Polystyrene and Polyacrylate-Based Cationic Copolymers

The cationic copolymers synthesized in our laboratory from different methods (emulsion, miniemulsion, and solution polymerization techniques) have several unique properties. First, they can form stable cationic colloidal particles. Second, the charge density of the colloidal particles can be well controlled. Third, the particle size can be very small (20-40 nm), which has not been reported before. These unique properties allowed us to look at different applications using these cationic colloidal particles. Polystyrene-based cationic colloidal particles were used as novel flocculants and paper sizing agents. Polyacrylate-based cationic polymers, which may form colloidal particles or may be soluble in water, were used as pressure-sensitive adhesives.

Cationic Colloidal Particle Flocculation Systems

Cationic polyelectrolytes, including linear, graft, and crosslinked polymers, have been used extensively in papermaking as retention aids [23-28]. The bridging formation is one of the most common mechanisms for fine and filler retention in papermaking. For an effective polymer bridging flocculation, the polymer must be adsorbed onto the substrate surface and the loops of adsorbed polymer molecules must be long enough to overcome the repulsion force between particles. The former requires a high charge density of polyelectrolyte to generate a strong attractive force between polymer and particle and the latter requires a low charge density of polyelectrolyte to form extended polymer loops. Both theoretical calculation [29] and experimental studies [30-32] indicated that high charged polymers adsorb in a flat rather than an extended conformation. Although low charged polymers initially tend to form bridge flocculation, they may get flat easily on the solid substrate under shear force.

Currently, dual retention systems are widely used in the paper industry. One of the dual systems involves a high cationic charge, low molecular weight coagulant and a low anionic charge, high molecular weight flocculant. The mechanism for the flocculation is that cationic polymer patches are first formed on the surfaces of negatively charged substrates, then the anionic polymers form bridges between these patches. Another dual retention system involves a cationically charged high molecular weight flocculant and an anionically charged colloidal particle such as bentonite and colloidal silica. In this system, the flocculation is induced by the sequential addition of a positively charged polymer followed by opposite charged colloidal particles [33-36]. A widely accepted flocculation mechanism for this system is that large flocs of fibers and fillers are first

formed by the bridging of cationic polymer, and then the flocs interact with negatively charged colloidal particles to form highly coagulated small flocs under high shear force. However, there are several problems in polymer flocculation under shear force. In addition to the polymer getting flat on a solid surface, the penetration of water-soluble polymer into the pores of the solid substrate, such as fiber, may significantly affect both the dynamics and efficiency of bridging flocculation or patch formation.

Potentially, cationic colloidal particle systems have advantages over traditional flocculation systems when used as retention aids or co-retention agents because: (1) there is no conformation change when the cationic colloidal particle 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 colloidal particles do not penetrate into the pores of the fiber surface due to their inflexible structure; and (5) there is no accumulation of colloidal particles in a closed water system because of the strong bonding force between cationic colloidal particles and negatively charged substances.

Cationic colloidal particle induced flocculation has been studied using the copolymeric particles synthesized in our laboratory [9,37]. These studies clearly showed that the positively charged small polystyrene particles could strongly bond to negatively charged large precipitated calcium carbonate and polystyrene latex, resulting in a particle bridging flocculation. Recently, Deng and Pelton [38,39] indicated that the colloidal particle bridging flocculation is more effective and less concentration dependent compared to the neutralization flocculation caused by a water-soluble polyelectrolyte. Rushmere [40] claimed the dual system of cationic silica and anionic polyacrylamide is an effective retention aid. Svending [41] described another dual system based on cationic silica and cationic polymer. In the past few years, we have done extensive research on the flocculation mechanism of the cationic colloidal particle systems. Our studies [37] have indicated that although cationic colloidal particles could form bridged flocculation, this system alone is not a very effective retention agent. However, the flocculation and retention efficiency could be significantly improved by combining the cationic colloidal particle with an anionic or cationic high molecule weight polyacrylamide (APAM or CPAM).

Figure 1 shows the effect of the cationic colloidal particle on the first-pass retention (FPR) of precipitated calcium carbonate (PCC) in bleached softwood kraft (BSK) pulp with or without polymers. The retention test of 0.1% PCC in 0.4% BSK pulp was conducted in a Dynamic Drainage Jar (%) with 39 nm cationic colloidal particles and a high molecular weight polymer [37]. It can be seen that the first-pass retention of PCC with 40 mg/L cationic colloidal particle is about 50%, and the maximum first-pass retention of PCC obtained by CPAM alone is about 60%. However, the PCC retention was greater than 95% when cationic particles were used in combination with APAM or CPAM.

Two types of patches (water-soluble cationic coagulant and water-insoluble cationic colloidal particle) are shown in Figure 2. The most effective bridge exists when the

cationic colloidal particle first adsorbs onto the PCC and fiber surface to form "patches," followed by the adsorption of APAM onto these cationic particle "patches." The main differences between these two types of patches are (1) the thickness of the "colloidal particle patches" is greater than the "polymer patches" because of the flat conformation of the latter on the PCC surfaces; (2) the charge neutralization can only happen at the immediately attached surfaces between the cationic colloidal particle and PCC, and the rest of the surface of the cationic colloidal particle can still remain a high positive charge; however, most of the charges in the backbone of the soluble polyelectrolyte are neutralized by negative charges on the PCC surface because the positively charged repeat units in polymer chains are directly bound on the PCC surface; and (3) the effectiveness of a polymer patch may change with time because of the penetration of flexible polymer chains into the pores of a solid surface, but the "colloidal particle patch" is less time dependent. It has been reported [42] that preaddition of cationic coagulants, such as poly(diallyldimethylammonium chloride) (poly-DADMAC), decreases the adsorption amount of high molecular weight CPAM on negatively charged suspensions while maintaining the flocculation efficiency because of the site-blocking effect. Compared to a water-soluble coagulant, the surface area of PCC occupied by adsorbed cationic colloidal particles has been found to be very small [9]. This is mainly because the cationic colloidal particle is rigid and it will not spread on the PCC surface during the adsorption. This suggests that the site-blocking effect for the cationic colloidal particle system is less important than a highly charged cationic water-soluble polymer, such as poly-DADMAC.

The significant improvement in flocculation shown in Figure 2 by the combination of a cationic colloidal particle and a cationic water-soluble polymer cannot be explained simply by the site-blocking effect. One important factor that affects the flocculation and retention is the conformation of the polymer on the surface of the suspension. Figure 3 illustrates the conformation of the CPAM on a solid surface in the absence and presence of cationic colloidal particles. It is generally known that the flocculation efficiency is dominated by the conformation of flocculant on the substrate surface if other parameters remain the same. In the absence of cationic colloidal particles, the cationic polymer will easily get flat on a negatively charged surface, and therefore the length of the polymer loop is short. However, in the presence of cationic colloidal particles, the repulsion force between cationic colloidal particle and cationic polymer will prevent the polymer from getting flat on the substrate surface. As a result, the polymer extrudes into liquid to form more effective bridges and thus gives better flocculation and retention.

If the proposed mechanism is correct, the addition order of the cationic colloidal particle and CPAM should significantly affect the flocculation efficiency. Figure 4 shows the flocculation results obtained by the same dual cationic retention system but in different addition orders. A lower retention was obtained when CPAM was added first. It is obvious that when CPAM was added first, the addition of cationic colloidal particles should not significantly affect the conformation of CPAM. As a result, the retention efficiency was reduced.

The effect of the colloidal particle size on flocculation and retention also supported the proposed mechanism. Figure 5 shows that the first-pass PCC retention obtained by CPAM was significantly improved by addition of cationic colloidal particles with a particle size less than 50 nm, but was not enhanced if particle size of the cationic colloidal particles was larger than 100 nm. According to the flocculation mechanism (see Figure 3), the ratio of polymer chain length to particle diameter is a dominating factor for CPAM-cationic colloidal particle dual system. If the polymer chain length is much longer than the diameter of cationic colloidal particles, the polymer may bond to another solid surface leading to effective flocculation. In contrast, if the polymer chain length is less than the diameter of the cationic particle, it is impossible for polymer to form a bridge between two suspended solid particles.

Cationic Colloidal Particle as a Paper Sizing Agent

Sizing is a process to increase paper hydrophobicity and water resistance. It is generally accepted that to be a good sizing agent, a material must have high retention on fibers, be uniformly distributed on fiber surfaces, be able to produce hydrophobic fiber surfaces, adhere strongly to fibers, be chemically inert, and ideally have no adverse effects on the papermaking process and paper properties. Currently, alkyl ketene dimers (AKD), alkenyl succinic anhydride (ASA), and rosin are the most common sizing agents used in papermaking. However, none of them can fully satisfy the papermaker's requirements. It is well known that rosin-based sizing agents are restricted only to be used in acidic conditions. Although AKD and ASA can be used for alkaline papermaking, some problems, such as paper slipperiness, low emulsion instability, hydrolysis, deposition on the paper machine, and sizing reversion, often occur during papermaking.

Polymeric cationic internal sizing agents, such as cationic polystyrene latexes [3-5], polystyrene acrylic acid ester [43], and cationic vinyl polymers [44] have been developed recently. One of the advantages of these cationic polymeric sizing agents is that no retention aid is needed during the sizing development. Furthermore, the cationic polymeric sizing agent will reduce the total cationic charge demand of a pulp furnish. In addition to the paper sizing development, improvements in paper strength and optical properties were also observed in previous studies [3-5]. However, a large amount of cationic polymeric sizing agent (5% based on dry fibers) is required in order to obtain a reasonable sizing degree [5].

In order to get a uniform distribution of cationic particles onto fiber surfaces, the particle size must be very small. In addition, these particles should be able to attach to fibers and form a hydrophobic barrier. Polystyrene-based cationic copolymer (PSCC) prepared from solution polymerization could meet these requirements well. First, cationic repeat units along the polymer molecule could serve as a retention aid. Second, polystyrene could provide high hydrophobi-city. Finally, the uniform distribution could be achieved through the small particles whose sizes can be controlled by charge density. The performance of polystyrene-based cationic colloidal particles as a sizing agent was evaluated by the Hercules Sizing Test (HST) as reported previously [45]. Figure 6 shows the sizing effect of the PSCC with 10% cationic comonomer (particle size 30 nm). It can

be seen that the sizing efficiency was increased sharply when the addition level of polymer increased from 0.3% to 0.5%. The results indicated that a very small amount of PSCC with 10% cationic comonomer could give effective sizing.

Figure 7 shows the effect of particle size on the sizing efficiency. PSCC that had 10% charge density was used to test the effect of particle size on sizing. In order to obtain different particle sizes, the same polymer was dispersed in water at 80, 90 and 100°C, respectively. The sizing efficiency was increased as particle size was reduced. It is believed that the spreading of the colloidal particles on the fiber surface during the curing process is important. The smaller the particle, the more readily the polymer spread fully on the fiber surface. As a result, better sizing was achieved. Comparing these results with those reported by Inoue, et al. [5], it may be suggested that the particle size of the colloidal particle is a critical factor in controlling sizing efficiency.

Cationic Water Soluble/Dispersible Pressure-Sensitive Adhesives

Pressure-sensitive adhesives (PSAs) are widely used for self-adhesive stamps, tapes, labels, and paper coating. It is well known that PSAs have long been a problem as "stickies" contaminants for paper recycling mills. The main problems associated with stickies include deposition on the felts, press rolls, and drying cylinders, which creates problems with paper formation, reducing paper quality and paper machine runnability. The annual cost of stickies to the U.S. paper industry is estimated to be about $600 to $650 million [46].

The technologies currently being evaluated by adhesive manufacturers in an effort to make repulpable adhesives can be divided into two categories, i.e., recoverable (or screenable) and dispersible/soluble adhesives. Two different approaches have been employed in recoverable adhesive development: (a) the adhesives that have a high glass transition or melting temperature, and will not soften and break down under repulping conditions; and (b) the adhesives that have a density significantly lower or higher than water and fibers. Unfortunately, high glass transition or melting temperature polymers can only be used for hot-melts but not for PSAs. Although some high or low-density polymers have been used for PSAs, there are only a limited number of polymers that can meet this unique requirement. In contrast to the recoverable PSAs, water-soluble/dispersible PSAs have been developed. These adhesives include acrylic or acrylate copolymers modified with hydrophilic components such as starch, sugar, carboxylic acids, polyglycols, maleic acid, etc. Although these water-soluble adhesives will not form stickies during recycling, the accumulation of water-soluble adhesives in paper process water is still an unsolved problem. Therefore, a water-soluble/dispersible pressure-sensitive adhesive that can be easily removed from process water is desirable.

We have recently developed polyacrylate-based cationic water-soluble/dispersible pressure-sensitive adhesives [12,22]. The cationic PSAs have many advantages compared to conventional PSAs. First, they can be dissolved or dispersed in water by controlling the cationic charge density in the polymer backbone and will not form stickies during repulping and papermaking processes. Second, they can be easily removed from

the system by adsorbing onto fiber and fine surfaces because they are cationically charged. Table 3 shows the adhesive properties of several water-soluble/dispersible cationic PSAs and commercial PSAs. It can be seen that the cationic-water soluble/dispersible PSAs have comparable adhesive properties. Repulping tests indicated that over 97% of the cationic PSA could be absorbed onto the fibers when the PSA content in the recycled paper was 0.5%. No stickies were found in the recycling process.

Conclusions

Polystyrene-based cationic copolymers with different charge densities and colloidal properties could be synthesized by emulsion and solution polymerization techniques. The copolymers could form stable colloids in water if the charge balance is well controlled.

Cationic polymeric colloidal particles could form bridge flocculation. The combination of cationic polymeric colloidal particles with a cationic or anionic polymer can significantly improve the flocculation efficiency. For the dual-flocculant system of a cationic colloidal particle and anionic polymer, the cationic colloidal particle may first form cationic patches on the substrate surface, and then the anionic polymer forms bridges through these patches. For the dual-flocculant system containing cationic colloidal particles and cationic water-soluble polymer, the preadsorption of cationic colloidal particles may affect the conformation of the polymer on the substrate surface. The charge repulsion between preadsorbed cationic colloidal particle and cationic water-soluble polymer may prevent the polymer from getting flat on the substrate surface; thus the flocculation efficiency of cationic water-soluble polymer can be significantly improved through more effective bridge flocculation. Cationic polymeric colloidal particles can also function as effective sizing agents. Smaller particles contribute to a higher sizing level in terms of better spreading. Polyacrylate-based cationic pressure-sensitive adhesives could be water soluble/dispersible, and would reduce the problem of stickies in paper recycling.

Acknowledgment

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Table 1. Emulsion Polymerization Conditions and Particle Colloidal Properties.

Sample	A	B	C	D	E
Styrene (mol)	0.108	0.108	0.108	0.108	0.108
MAPTAC (mol)	0	0	0	0.0019	0.0082
Surfactant (mol)	0	0.003	0.0089	0.0089	0.0089
Water (L)	0.15	0.15	0.15	0.15	0.15
VA-044 (mol)	0.0007	0.007	0.0007	0.0007	0.0007
DVB (mol)	0.0043	0.0043	0.0043	0.0043	0.0043
Particle size (nm)	364	100	28.7	33.9	39.0
Polydispersity	-	-	0.17	0.24	0.41
Charge density (μeq/m^2)	-	-	2.84	3.04	3.44

Table 2. Water solubility of the poly(styrene-co-VBTMAC)s.*

Sample	Cationic content (mol%)	Particle size (nm)							
		25°C	40°C	60°C	70°C	75°C	80°C	90°C	100°C
E	5	-	-	-	-	-	47	41	40
F	10	-	-	-	-	56	47	30	30
G	15	-	-	92	34	+	+	+	+
H	20	-	51	+	+	+	+	+	+
I	30	+	+	+	+	+	+	+	+

*Solution was prepared by mixing 1 g copolymer in 1 liter water for 1 hr at the fixed temperature, then the solution was cooled to room temperature. The particle size was measured at 25°C. "-" indicates unstable dispersion, "+" indicates full dissolution.

Table 3. Adhesive properties of water soluble/dispersible PSAs.

Sample	Cationic content (mol%)	Cross-link degree (mol%)	Water solubility at 50°C	Adhesive properties	
				Shear (min.)	Peel (oz/in.)
PSA1	10	0	Dispersible (<1.5 μm)	26	18.8
PSA2	15	0	soluble	59	5.5
PSA3	15	0.2	soluble	342	7.8
PSA4	15	0.5	Soluble	>40 h	3.6
PSA5	20	0	soluble	166	2.5
Com1 [a]	0	-	no	232	9.4
Com2 [b]	0	-	no	219	33.2
Com3 [c]	0	-	no	<0.1	0.28

[a] Commercial polyacrylic-based PSA. [b] Nonpeelable general post label. [c] Peelable label
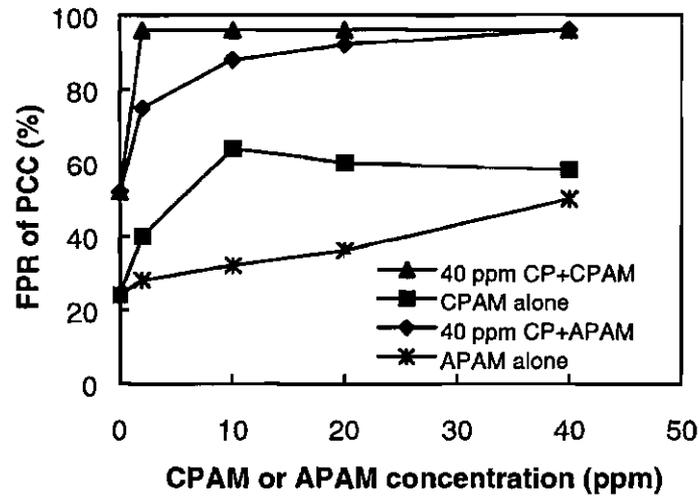
Figure 1. The first-pass retention of PCC in wood pulp as a function of polymer (CPAM or APAM) concentration in the presence and absence of cationic colloidal particles.
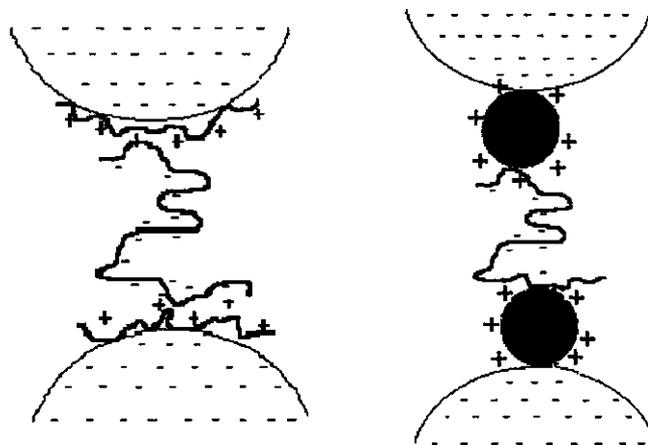

Figure 2. Flocculation by bridge formation between cationic patch and anionic polymer. (A) For low molecular weight polymer, most of the charges are neutralized because the polymer flattened on the negatively charged suspension surface. (B) For cationic colloidal particle, only the charges that immediately attached to the negatively charged suspension surface are neutralized.
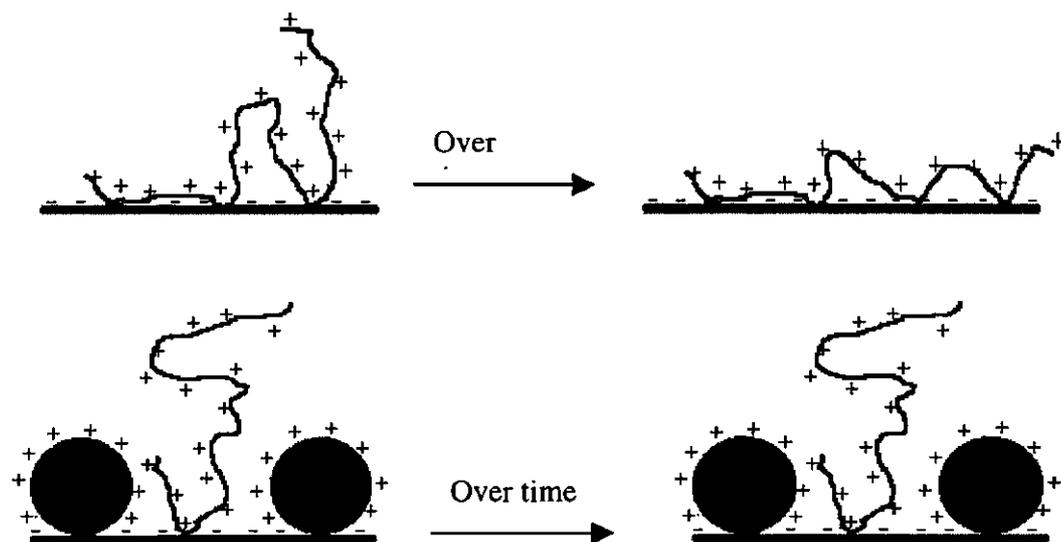
Figure 3. Proposed conformation of cationic PAM at a negatively charged solid surface in the presence and absence of cationic colloidal particles.
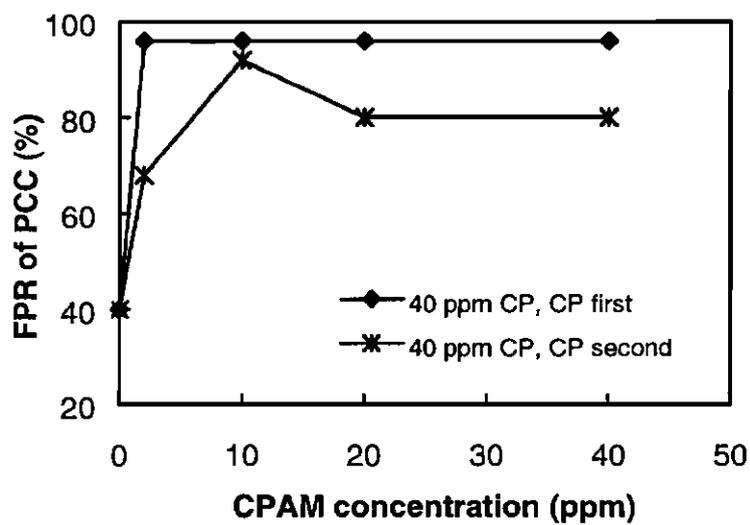

Figure 4. The effect of polymer addition sequence on the PCC retention using a CP CPAM dual retention system.
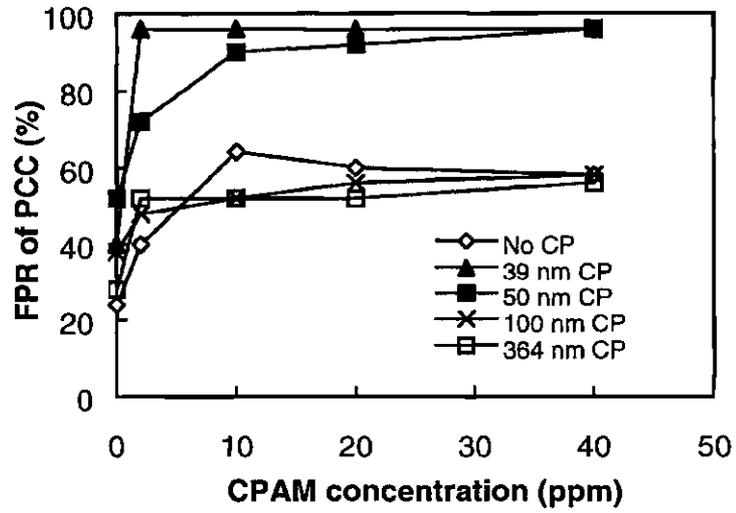
Figure 5. The effect of colloidal particle size on the PCC retention when CPAM was used as a coflocculant.
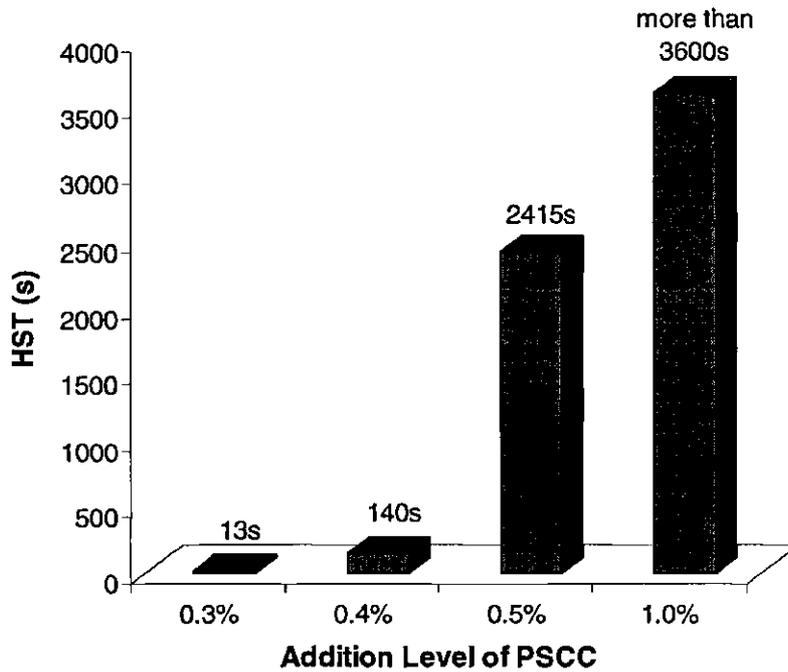

Figure 6. Sizing development with PSCC. PSCC: 10% cationic comonomer; curing: 140°C for 30 minutes.
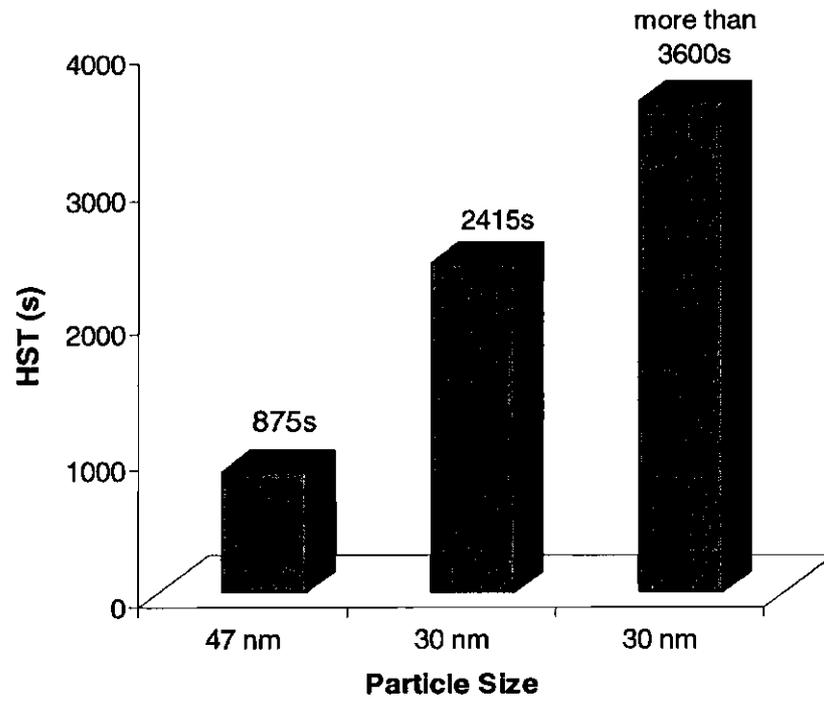
Figure 7. Effect of particle size on sizing. PSCC: 10% cationic comonomer; addition level: 0.5%; curing: 140°C for 30 minutes.