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Cationic Microparticles in Papermaking Wet End

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1. Introduction

The term microparticle has been widely used in the paper industry for more than two decades. Broadly speaking, any material in a fine particulate form with a size in the micro- or nanometer range may be called a microparticle. Paper fillers, such as clay, ground calcium carbonate (GCC), precipitated calcium carbonate (PCC), talc, and titanium oxide, are all microparticles. However, for papermakers, the term microparticle is often used for microparticle retention systems that can improve filler and fines retention, drainage, and paper formation. These microparticles include negatively charged colloidal silica and amphoteric charged bentonite [1-4]. In papermaking, chemical additives have to directly or indirectly interact with pulp fibers. Because pulp fiber is negatively charged, anionic and amphoteric microparticles cannot have effective interactions with the pulp fiber. Thus, these microparticle retention aids have to be used in conjunction with water-soluble cationic polymers such as polyacrylamide and cationic starch. On the contrary, cationic microparticles can directly adsorb on negatively charged fiber and fine surfaces and thus may be used as a single chemical additive to improve the papermaking process and paper properties.

Cationic microparticles are not new for papermakers. For example, PCC fillers, polyaluminum sulfate, cationic emulsion of sizing agents, cationic latex for paper coating, and polymeric cationic microparticle retention and sizing agents are all cationic microparticles in nature although people do not use the term microparticles for some of them. These cationic microparticles can be grouped as inorganic cationic microparticles and polymeric cationic microparticles.

This paper will focus on the cationic microparticles that have been used as flocculants, retention agents, strength agents, and sizing agents for papermaking. Both polymeric and inorganic cationic microparticles will be covered. The synthesis and colloidal properties will be briefly discussed, and the potential applications of these cationic microparticles in the paper industry will be discussed in detail.

The charge characteristics of microparticles in water are pH dependent. Inorganic fillers are positively charged at low pH, but negatively charged at high pH [5]. The charges on the particle surface are also influenced by polymer adsorption. In this way, the fillers can be modified with either cationic or anionic polymers [6,7]. Although cationically charged fillers can be regarded as cationic microparticles, they are used as raw materials rather than papermaking processing additives. Thus, fillers will not be the focus of this article.

2. Inorganic Cationic Microparticles in Papermaking

2.1. Inorganic Cationic Microparticles as a Single Additive

Aluminum sulfate, commonly called alum, is one of the most important papermaking chemicals. It is well known that alum is fully soluble in water at low pH, but forms colloidal particles (aggregates with different species, charges, and chemistries) with broad particle size distribution at pH 4-8 [8-10]. Although aluminum salts, such as aluminum sulfate, polyaluminum chloride (PAC), polyaluminum sulfate, polyaluminosilicate, and sodium aluminate, are often used in the form of cationic aggregates in papermaking, papermakers do not widely refer to them as cationic microparticles.

For a long time, cationic alumina microparticles formed from aluminum salt solutions have been widely used as charge control agents, retention aids, rosin sizing emulsifiers, and water clarification flocculants [11]. Because both water-soluble aluminum ion species and colloidal particles are usually present in water simultaneously, it is very

difficult to separate the roles of water-soluble aluminum species and insoluble particles in papermaking systems. Generally speaking, water-soluble cationic aluminum species contribute most in charge control (reducing cationic demand, adsorbing on fiber, fines, and filler surface, etc.), particle stabilization (rosin size stabilizer) and destabilization (reducing double-layer thickness of solid surface), neutralization of negatively charged polymers (anionic trash), and as fixation agents (improving rosin sizing efficiency, fixing anionic trash onto fiber surface). Contrary to the water-soluble cationic species, the cationic particles formed by aggregates of aluminum species contribute most to the flocculation of fine particles (such as in water treatment) and adsorbent and absorbent (such as in dye and anionic trash removal). Although alum can also improve the water drainage rate of paper machines, it is not clear if these improvements should be attributed to cationic water-soluble species, colloidal cationic alumina microparticles, or both.

2.2. Inorganic Cationic Microparticle-Based Dual System

Traditionally, papermakers use a water-soluble cationic polymer rather than insoluble particles to improve retention [12-18]. The bridging formation caused by water-soluble cationic polymers 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 [19] and experimental studies [20-22] indicate that highly charged polymers adsorb in a flat rather than an extended conformation. Although low charged polymer initially tends to form bridge flocculation, it may become flat easily on the solid substrate under shear force. Furthermore, the penetration of water-soluble polymer into the pores of the solid substrate, such as wood fibers, may significantly affect both the dynamics and efficiency of bridging flocculation or patch formation.

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 flocculation system involves a cationically charged high molecular weight flocculant and anionically charged colloidal particles 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 [1-4]. 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.

Similar to anionic microparticle retention systems with a colloidal particle used in conjunction with a water-soluble cationic polymer, cationic microparticle-based dual retention systems have been studied recently. Cationic alumina particles and cationic silica sols are two typical inorganic cationic microparticles that have been used in conjunction with a water-soluble polymer as a dual retention system. Potentially, a cationic microparticle retention system has some advantages over traditional flocculation systems when it is used as a retention aid or coretenion aid because: (1) there is no conformation change when the cationic microparticle adsorbs onto a negatively charged substrate, which may result in a more effective patch formation; (2) the total cationic demand of the pulp furnish in papermaking can be reduced; and (3) there is no accumulation of microparticles in a closed water system due to the strong bonding force between cationic microparticles and negatively charged substances.

Smith [23] studied the retention of fillers by sequential addition of a cationic coagulant, an anionic flocculant, and then pre-prepared cationic alumina microparticles, such as hydrolyzed or precipitated aluminum sulfate, polyaluminum chloride (PAC), polyaluminum sulfate, polyaluminosilicate, and sodium aluminate, with particle sizes varying from 1 to 300 nm. The cationic coagulant was first added to neutralize the pulp

furnish and provide cationic patches or anchoring points for the anionic flocculant. Then the anionic flocculant was added to form large flocs. Finally the cationic microparticles were added under shear. The addition of cationic microparticles has led to improved drainage, paper formation, and product porosity with high retention efficiency. The mechanism of this retention system may be similar to the cationic flocculant/colloidal silica system. Ovenden [24] studied the retention aid system of cationic alumina microparticles and anionic polymer. It was found that filler flocculation was very effective when the cationic microparticles were used in conjunction with an anionic polyacrylamide of high molecular weight and low charge density, and the retention system was insensitive to shear stress and pH from 6-8. Carré [25] studied the starch and alumina-based microparticle retention systems in a wide pH range. The following results were found: (1) PAC or alum can only interact with the starch which contains anionic groups. The addition of PAC or alum in neutral or alkaline pulp leads to precipitates of aluminum hydroxide, which remain cationic during the first few minutes. The transient cationic microparticles destabilize the fillers, fines, and fibers, which are then flocculated when a starch containing anionic groups is added. (2) At acid pH, the transient cationic precipitates of aluminum hydroxide can only be formed with an alkaline source of aluminum, such as sodium aluminate. An acid solution of aluminum can be detrimental to both retention and drainage with this retention system. (3) The retention system of cationic microparticles and starch is not sensitive to a high content of calcium, while the retention system of an anionic microparticle and a cationic polymer becomes sensitive when Ca^{2+} content is above 200 mg/L.

Cationic silica sol has also been used as a cationic microparticle retention aid. Cationic silica sols are prepared from colloidal silica sols by reacting with a polyvalent metal salt to give the sol particles a positive surface charge [26,27]. The polyvalent metal salt is usually an aluminum salt. The particle size of the cationic sols is normally in the range of 2 nm to 100 nm. The mole ratio of the cationic ion to surface silica is normally within the range of 1:2 to 2:1. The mole ratio of cationic ion to surface silica is calculated on the basis of 8 silicon atoms per nm^2 of silica surface [28]. The pH value of the cationic silica sol is about 5. Rushmere [29] claimed that the dual system of cationic silica and anionic

polyacrylamide (APAM) was very effective on filler retention at pH 4-9. The flocs exhibited enhanced resistance to shear force. He compared the effect of cationic silica sol with that of alum at different pH on retention and drainage. It was found that at pH 4, cationic silica sol with APAM improved retention and drainage significantly, but alum with APAM gave much less effect. At pH 8, both alum and cationic silica sol gave significantly improved retention and drainage when used with APAM. It is well known that alum will be mostly in microparticle form at pH 8, but in water-soluble form at pH 4. Rushmere's results indicated that cationic microparticles were better than cationic water-soluble alum in improving retention and drainage when used in conjunction with a water-soluble anionic polymer.

Svending [27] described another dual system based on cationic silica and a cationic polymer, such as cationic polyacrylamide (CPAM) or cationic guar gum. It was found that this retention system of two cationic components also gave improved retention and drainage at pH 4-9. The effect of addition order of the sol and the cationic polymer was investigated. It was found that for cationic sols of smaller particles (6 nm), a better effect is obtained if the cationic polymer is added first, while for cationic sols of larger particles (14 nm), a better effect is obtained when the cationic silica sol is added first. The reason for this is not clear. The new dual system of cationic silica sol with cationic polymer and the traditional dual system of anionic silica sol (5.5 nm) with cationic polymer were also compared. Results indicated that the dual system of cationic silica sol with cationic polymer improved drainage more effectively. The mechanisms contributing to the positive effect of the two cationic components were not studied. Svending suggested that the cationic silica sol partly neutralized dissolved anionic substances in the wood pulp and improved the strength of floc formed from the cationic water-soluble polymer. Thus, the flocculation efficiency of the cationic water-soluble polymer was improved, and the flocs became stronger.

3. Polymeric Cationic Microparticles for Papermaking

3.1. Synthesis of Polymeric Cationic Microparticles

In the past two decades, many polymeric cationic microparticles have been developed as papermaking additives. There are several advantages to using polymeric cationic microparticles compared to inorganic microparticles. First, the size, size distribution, and charge density of microparticles can be well controlled. Second, functional groups that may improve bonding, charge, and adsorption can be easily introduced to the microparticle surface during polymerization or modification. Third, the polymeric cationic microparticles can be hard, soft, swellable particles if different polymers are used. The melting or glass transition temperature of the polymeric cationic microparticles can also be controlled by using different polymers.

The cationic nature of the microparticles is generally achieved by using a cationic initiator and/or a cationic comonomer during polymerization, or by surface modification of polymeric microparticles. Alinec [30] first synthesized a series of cationic latexes as papermaking additives. In the study, a number of cationic latexes with different styrene (S)-butadiene (B) contents and 1% 2-(diethylamino)ethyl methacrylate quaternized by dimethylsulfate were synthesized by emulsifier-free polymerization. The mixture of styrene and butadiene was chosen because, by changing their ratio, latex with different softness can be obtained. Polymerization was carried out at 60°C for 8 hr using H₂O₂ and Fe(NO₃)₂ as initiators. The sizes of the particles are between 120 and 160 nm depending on the synthesis chemistry with reasonable monodispersity.

The efficiency of cationic microparticles as papermaking additives does not only depend on the charge characteristics but also the size of the microparticles. Microparticles with smaller sizes should distribute more evenly on the fiber surface and have better spreading during heating. Deng and a coworker [7] have synthesized a range of cationic polymeric microparticles with different particle sizes using emulsion and microemulsion polymerization techniques. Styrene, methacrylamidopropyltrimethyl-ammonium chloride (MAPTAC), and divinylbenzene (DVB) were used as hydrophobic backbone, cationic comonomer, and crosslinker, respectively. 2,2'-Azobis(N,N'-dimethyleneisobutyramidine) dihydrochloride (VA-044) was used as a cationic initiator and

cetyltrimethylammonium bromide was used as a cationic surfactant. The properties of the colloidal particles prepared are given in Table 1.

It was found that the size of the colloidal particles prepared from microemulsion polymerization was a function of the concentrations of surfactant and cationic monomer. 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 when the charge density of the copolymer is high. Furthermore, when high cationic monomer was added, the emulsion was not stable and there were two fractions (high and low charge density fractions) in the final products. Although the microemulsion technique can be used to prepare very small microparticles (<100 nm), the remaining surfactant used in polymerization will negatively affect the application of polymeric microparticles. To remove cationic surfactant from the final latex is difficult and high in energy cost, particularly when the particles are very small. To solve this problem, Deng et al. [31-33] recently prepared very small (<100 nm) cationic polymeric microparticles using solution polymerization followed by self-assembly in water. The main advantages of the copolymers from solution polymerization are: (1) no emulsifier is needed; (2) copolymers with different charge contents can be easily obtained; and (3) the colloidal particle size can be easily controlled by both the charge density and copolymer dispersing temperature.

3.2. Polymeric Cationic Microparticles as Retention Aids

There are several advantages of using polymeric cationic microparticles instead of inorganic cationic microparticles as retention aids. First, polymeric microparticles have the potential to improve paper properties while increasing retention. It is the papermaker's intention to increase the filler content in the paper. But several problems limit the amount of filler that can be introduced. Among them are the detrimental effects on tensile strength and pick resistance caused by the interference of the filler particles on fiber-fiber bonding. Sizing efficiency is also reduced, and poor attachment of the filler

particles may cause dusting at high filler content. Alinec [34] studied the retention of clay with cationic styrene-butadiene latex. Results showed that, other than increased filler retention, the tensile strength and sizing performance of the paper were improved as well. Second, polymeric cationic microparticles may be used in a broad pH range. Because of the chemical nature of aluminum salt, inorganic cationic microparticles may easily lose cationicity in alkaline conditions. But polymeric cationic microparticles can maintain cationic charge even at pH 9.5 [34].

Polymeric cationic microparticle-based retention systems have been well studied by Deng and coworkers [7,35]. Figure 1 shows the effect of the polystyrene-based cationic microparticle (CMP) 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 microparticles and a high molecular weight polymer. It can be seen that the first-pass retention of PCC with 40 mg/L cationic microparticles alone 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 [36] 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 pre-adsorbed cationic colloidal particles has been found to be very small [7]. 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 1 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.

The flocculation mechanism was supported by the addition order of the retention aids. Figure 4 shows the retention results obtained by the dual cationic retention system with different addition orders. A lower retention was obtained when CPAM was added first.

It is obvious that when CPAM is added first, the addition of cationic microparticles should not significantly affect the conformation of CPAM. As a result, the retention efficiency was reduced.

The effect of the 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 microparticles with a particle size less than 50 nm, but was not enhanced if particle size of the cationic microparticles 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 a CPAM-cationic microparticle dual system. If the polymer chain length is much longer than the diameter of cationic microparticles, 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 microparticle, it would be difficult for the polymer to form a bridge between two suspended solid particles. This phenomenon is illustrated in Figure 6.

3.3. Polymeric Cationic Microparticles as Binding Agents

The use of cationic polymer latex as a binding agent has been extensively studied by Alinec and coworkers [30,34,37]. Cationic latexes with different styrene/butadiene ratios were used as papermaking additives to make handsheets. The latex addition levels were 2, 5, and 10% of the fibers. After drying at temperatures above the film-forming temperature, the latexes formed a film on the handsheets. The process is shown in Figure 7. The effect of the latexes on handsheet properties was investigated and the results are shown in Figure 8. All three film-forming styrene-butadiene latexes improved the tensile strength of the handsheet, and the performance increased with polymer softness. However, the nonfilming pure styrene latex interferes with the development of fiber-fiber bonds, and the mechanical properties suffer. When the handsheets containing 10% pure polystyrene latex were treated at 150°C in a press (10 atm) to cause the latex to form a film, the tensile strength of the handsheets became similar to those treated with the styrene-butadiene latexes. It is suggested that the role of the polymer film is to fill in the

areas of surface roughness on the fiber, to provide for a large area of molecular contact between fibers, and to improve the transfer of stress between fibers. The main contribution of the latex in improving strength is the increase in bonded area. It has also been found that the latex was most effective in enhancing interfiber bonding when deposited on fibers in the form of a monolayer. If the latex is destabilized and forms aggregates on the fiber surface, the effect on improving the paper mechanical properties will be reduced.

Generally, an increase in paper tensile strength obtained by fiber refining is accompanied by decreased opacity. Higher tensile strength means higher bonded area and lower unbonded area. The unbonded area is the fiber air interface where the scattering of light takes place. Lower unbonded area means lower opacity. But when cationic microparticles were used as binders to increase the paper strength, the opacity of the paper did not decrease. This phenomenon has been explained by Alince [37]. For fiber-fiber binding, the contact between fibers must be on a molecular level (less than 1 nm). To affect light scattering, the fibers need to be in optical contact, which means the fiber can be separated by a distance in the order of the wavelength of light (several hundred nanometers). When the cationic microparticle forms a transparent film on paper, it fills the optical contact area, but does not change the optical area between fibers. In filling the optical area, it increases the area of molecular contact and thus increases the paper strength.

The use of cationic microparticles as binding agents has also been disclosed in several patents [38-44]. It was reported that the cationic microparticles could increase both the dry and wet strength of the paper and thus could be used as additives to prepare wood fiber-based fabrics and used in the production of highly filled paper and composites. Because the cationic microparticles contain ammonium groups, the fabric would have an antistatic effect.

3.4. Cationic Microparticles as Sizing Agents

Sizing is a process to increase paper hydrophobicity and water resistance. Currently, alkyl ketene dimers (AKD), alkenyl succinic anhydride (ASA), and rosin are the most common sizing agents used in papermaking [45,46]. However, none of them can fully satisfy the papermaker's requirements. It is well known that rosin-based sizing agents are restricted to use only 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 the papermaking process. These sizing agents also have an adverse effect on paper strength.

The use of polymeric cationic microparticles as sizing agents was first reported by Killam [47]. Cationic microparticles containing vinylbenzyltrialkyl ammonium salt, such as dimethylstearyl-4-vinylbenzylammonium chloride, were synthesized from emulsion polymerization. Dimethylstearyl-4-vinylbenzylammonium chloride acted as a polymerizable comonomer as well as a surfactant. The sizing performance of the polymeric cationic microparticles with an addition level of 0.5% based on dry fiber was found to be comparable to that of rosin.

Ohmori [48] reported using polystyrene acrylic acid ester-based cationic microparticles as sizing agents to prepare ink-jet recording paper. The recording paper has a homogenous image quality, a high recording density, excellent ink absorbency for full-color recording, and little show-through or strike-through. Moreover, the ink absorbency of the sheet does not decrease after storage. Muller [49] used cationic vinyl polymer dispersions as both internal and surface sizing agents.

The performance of cationic microparticles as internal sizing agents has been extensively studied by Deng and coworkers [32,33]. Polystyrene-based cationic microparticles as sizing agents were evaluated by the Hercules Sizing Test (HST). Figure 9 shows the sizing effect of the polystyrene cationic microparticles with 10% cationic comonomer

(particle size 30 nm). It can be seen that the sizing efficiency increased sharply when the addition level of polymer increased from 0.3% to 0.5%.

Figure 10 shows the effect of particle size on the sizing efficiency. Polystyrene cationic microparticles that had 10% charge density were used to test the effect of particle size on sizing. In order to obtain different particle sizes, the cationic polystyrene copolymer was dispersed in water at 80, 90 and 100°C to form self-assembly microparticles. The cationic microparticle particle size prepared in this way was in the range of 30-50 nm. 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.

The effect of the cationic microparticle sizing agent on paper properties was also studied. It was found that the addition of cationic microparticles improved both the opacity and tensile strength of the handsheet. The results further prove that polymeric cationic microparticles are multifunctional papermaking additives.

4. Summary

The cationic microparticle is a unique form of material for the paper industry. It has the advantage of ready deposition on anionic fibers because of electrostatic attraction. Because of its cationic charge, it can interact with other anionic substances in the papermaking system as well. Inorganic cationic microparticles, such as aluminum salt and colloidal cationic silica, can be used as retention aids to improve fines and fillers retention. Aluminum salt can also be used as a fixation agent, charge neutralizer for wet-end control, coagulant for wastewater treatment, etc. Because of the chemical nature of aluminum salt, inorganic cationic microparticles normally can only be used at neutral or acidic conditions. Organic cationic microparticles are multi-functional additives for papermaking in a broad pH range. They have the ability to improve retention, sizing, tensile strength, and opacity of the paper simultaneously. To be more effective as a

retention aid, sizing agent, and binding agent, microparticles should be stable enough to prevent aggregation, and the particle size should be ideally less than 100 nm. Smaller sized stable latex would be able to distribute more evenly on the fiber surface and thus give better performance. Functional cationic microparticles may be able to give added performance. Reactive groups on the latex may further improve the paper strength. Cationic ammonium groups have an antistatic effect. Cationic microparticles, especially polymeric microparticles, should have great potential in the paper industry.

References

1. L. Wägberg and T. Lindström, *Nordic Pulp Paper Res. J.*, 2, 49 (1982).
2. L. Wägberg, X.P. Zhao, I. Fineman and F.N.L. Li, *Tappi J.*, 73(4), 177 (1990).
3. L. Allen and I. Yaraskavitch, *Tappi J.*, 74(7), 79 (1991).
4. A. Swerin, U. Sjodin and L. Odberg, *Nord. Pulp Paper Res. J.*, 8, 389 (1993).
5. L. Neimo, "Papermaking Chemistry", L. Neimo, Ed., Fapet Oy, Helsinki, Finland, 151 (1999).
6. B. Alince and P. Lepoutre, *Tappi J.*, 1, 92 (1983).
7. H. Ono and Y. Deng, *J. Colloid Interface Sci.*, 188, 183 (1997).
8. T.R. Arnson, *Tappi*, 65(3), 125 (1982).
9. E. Strazdins, *Tappi*, 69(4), 111 (1986).
10. Y. Bottero and F. Fiessinger, *Nord. Pulp and Paper Res. J.*, 4, 81 (1989).
11. L. Neimo, "Papermaking Chemistry", L. Neimo, Ed., Fapet Oy, Helsinki, Finland, 95 (1999).
12. D. Eklund and T. Lindström, "Paper Chemistry," DT Paper Sci. Publ., Finland, (1991).
13. F. Lafuma, T. Wang, G. Durand and R. Audebert, *Colloids Surface*, 31, 255 (1988).
14. T. Wang and R. Audebert, *J. Colloid Interface Sci.*, 119, 459 (1987).
15. J. Gregory, *J. Colloid Interface Sci.*, 42, 448 (1973).
16. J. Gregory, *J. Colloid Interface Sci.*, 55, 35 (1976).
17. H. Tanaka, L. Ödberg, L. Wagberg and T. Lindström, *J. Colloid Interface Sci.* 134, 219 (1990).
18. M. Falk, L. Ödberg, L. Wagberg and G. Risinger, *Colloids Surface*, 40, 115 (1989).
19. J. Lyklema and G. Fleer, *Colloids Surface*, 25, 357 (1987).
20. R. Ruehrwein and D. Ward, *Soil Sci.*, 73, 485 (1952).
21. A. Michaels, *Ind. Eng. Chem.* 46, 1485 (1954).
22. T. Healy and V. Lamer, *J. Phys. Chem.*, 66, 1835 (1962).
23. J.H. Smith, Jr., *US Patent 5,221,435* (1993).

24. C. Ovenden, H.N. Xiao and N. Wiseman, *Tappi J.*, 83(3), 80 (2000).
25. B. Carré, *Nord. Pulp Paper Res. J.*, 8(1), 21 (1993).
26. E.P. Moore, Jr. and G. Vurlicer, *US Patent 3,956,171* (1976).
27. P.J. Svending, *US Patent 4,946,557* (1990).
28. R.K. Iler, *J. Colloid Interface Sci.*, 55(1), 25-34 (1976).
29. J.D. Rushmere and D.E. Wilmington, *U.S. Patent 4,798,653* (1998).
30. B. Alinec, M. Inoue and A.A. Robertson, *J. Appl. Polym. Sci.*, 20, 2209 (1976).
31. Y. Deng, Z. Yan and N. Yang, *Colloid Polym. Sci.*, 277, 227 (1999).
32. H. Ono and Y. Deng, *Engineering and Papermakers Conference*, Nashville, TN, 837 (1997).
33. N. Yang and Y. Deng, *J. Appl. Polym. Sci.*, 77(9), 2067 (2000).
34. B. Alinec, *Tappi J.*, 82(3), 175 (1999).
35. Z. Yan and Y. Deng, *Chem. Eng. J.*, 80, 31 (2000).
36. A. Swerin, G. Glad-Nordmark and L. Ödberg, *J. Pulp Paper Sci.*, 23, J389 (1997).
37. M. Inoue, B. Alinec, Y. Shao and T.G.M. van de Ven, *International Paper Coating Chem. Symp.*, Ottawa, Canada (1996).
38. R.A. Wessling, W.A. Foster and D.M. Pickelman, *US Patent 4,178,205* (1979).
39. D.M. Pickelman, W.A. Foster and R.A. Wessling, *US Patent 4,187,142* (1980).
40. W.A. Foster, D.M. Pickelman and R.A. Wessling, *US Patent 4,189,345* (1980).
41. K.B. McReynolds, *US Patent 4,255,383* (1980).
42. R.L. Post and R.G. Fort, *US Patent 4,445,970* (1984).
43. I. Noda, *US Patent 4,835,211* (1989).
44. H. Itoda, N. Watanabe and Y. Hosoya, *US Patent 5,250,602* (1993).
45. W. Scott, "*Principle of Wet-End Chemistry*", TAPPI Press, Atlanta, USA, 85 (1996).
46. L. Neimo, "*Papermaking Chemistry*", L. Neimo, Ed., Fapet Oy, Helsinki, Finland, 151 (1999).
47. S.H. Killam, *US Patent 4,017,440* (1976).
48. T. Ohmori, T. Yamagata, A. Ono and Y. Kojima, *US Patent 5,279,885* (1994).
49. M. Muller, J. Probst, H. Alberts, J. König, H. Baumgen and F. Puchner, *US Patent 5,314,721* (1994).

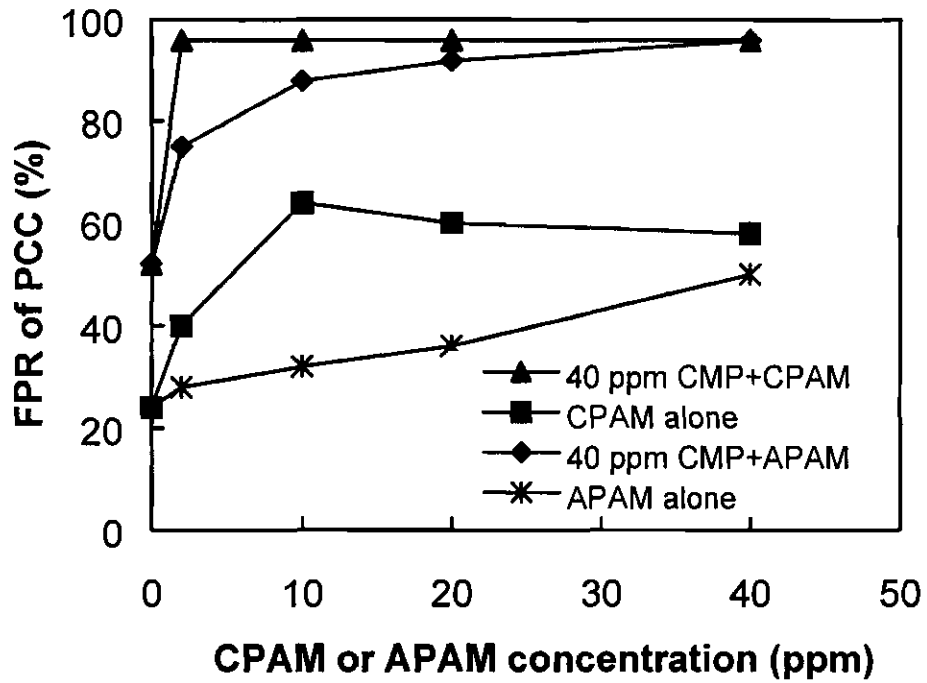


Figure 1. The first-pass retention of PCC in wood pulp as a function of polymer (CPAM or APAM) concentration in the presence and absence of cationic colloidal particles.

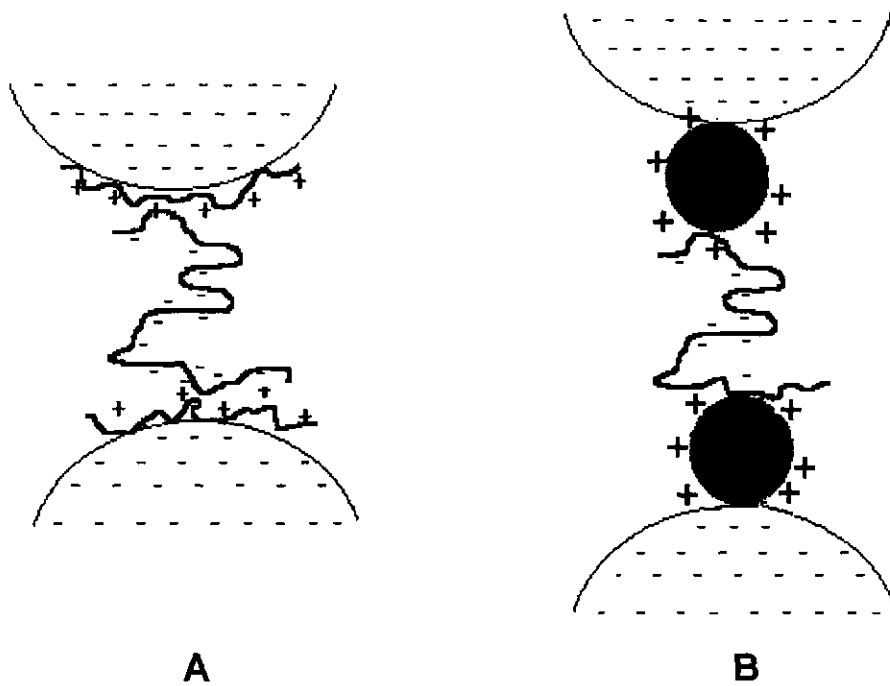


Figure 2. Flocculation by bridge formation between cationic patch and anionic polymer. (A) For low molecular weight polymer, most of the charges are neutralized because the polymer flattened on the negatively charged suspension surface. (B) For cationic colloidal particle, only the charges that immediately attached to the negatively charged suspension surface are neutralized.

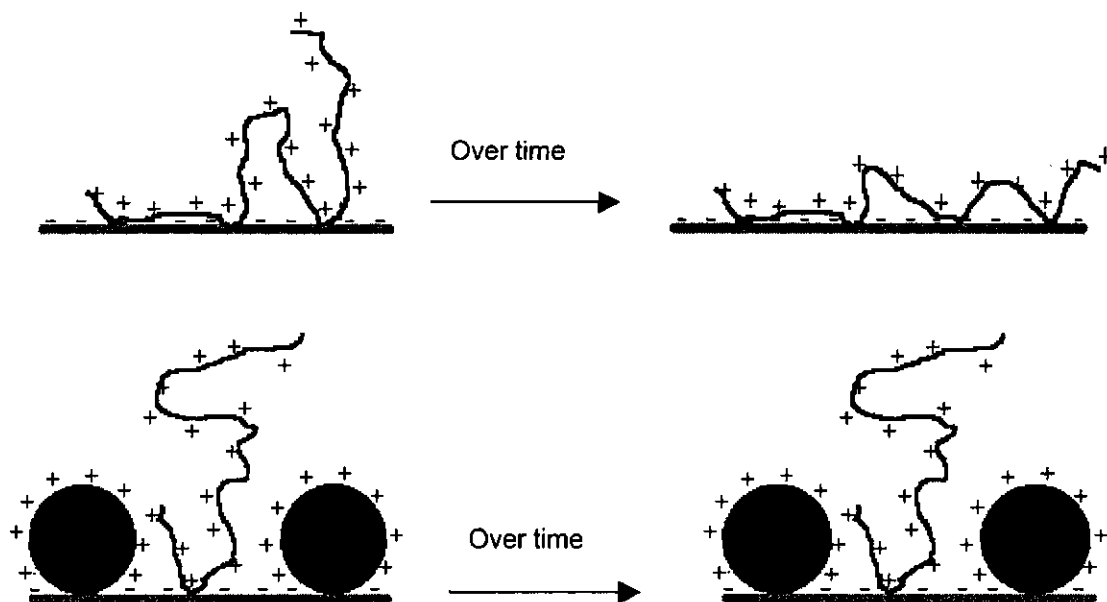


Figure 3. Proposed conformation of cationic PAM at a negatively charged solid surface in the presence and absence of cationic colloidal particles.

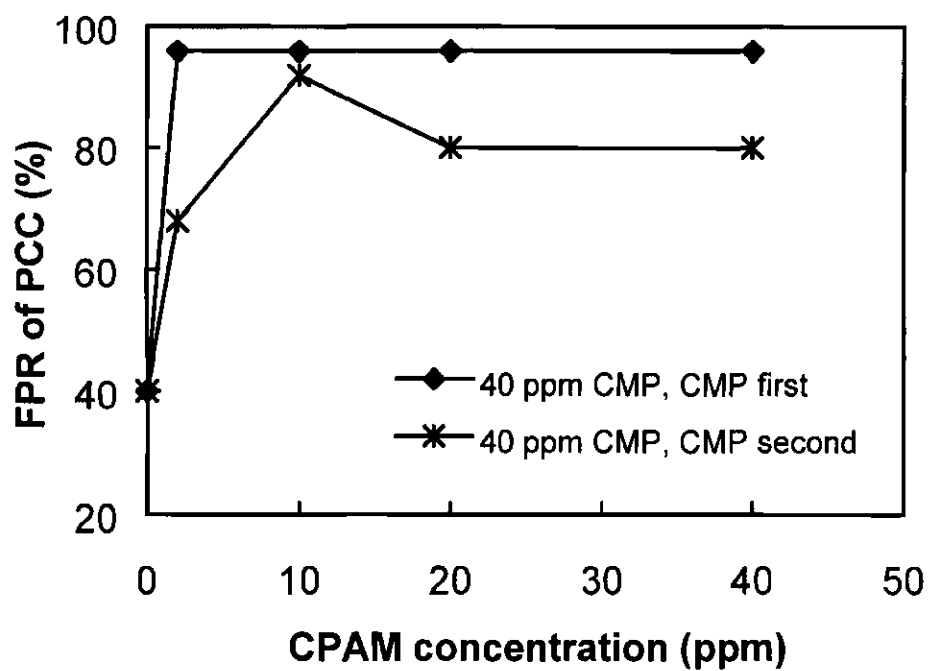


Figure 4. The effect of polymer addition sequence on the PCC retention using a CMP CPAM dual retention system.

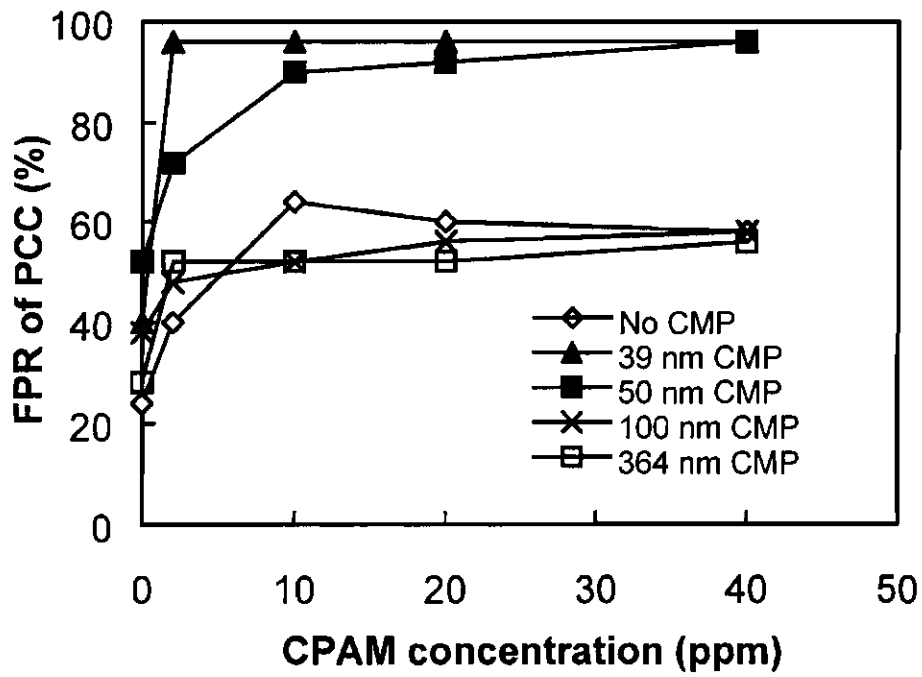


Figure 5. The effect of cationic microparticle size on the PCC retention when CPAM was used as a coflocculant.

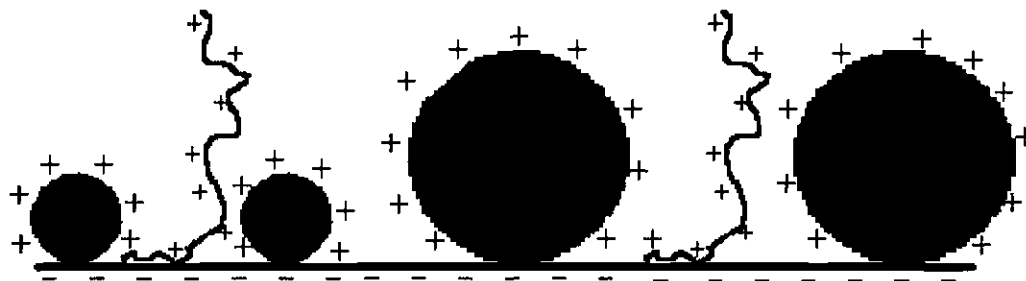


Figure 6. The effect of cationic microparticle size on the flocculation and retention using a CMP-CPAM dual retention system.

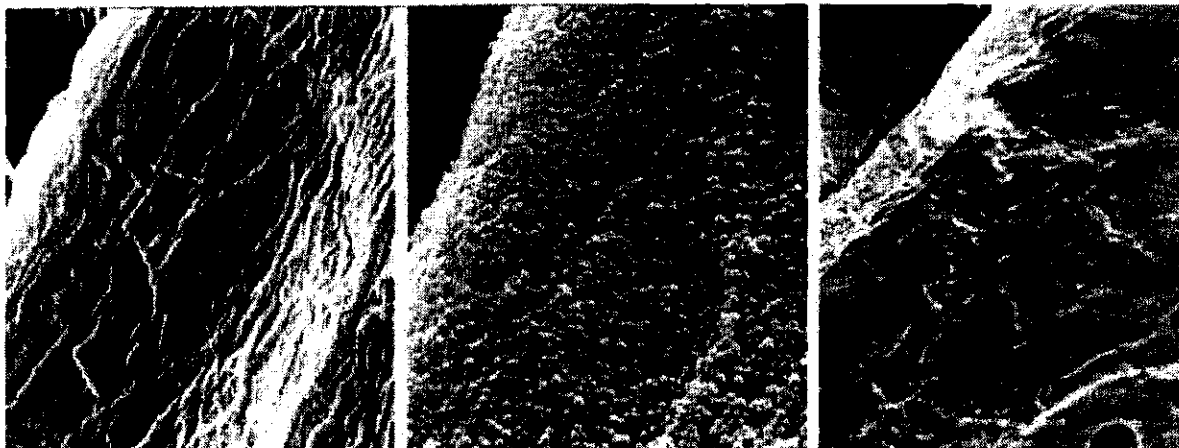


Figure 7. SEM photographs of the original fiber surface (left), coverage of fibers by deposited latex (middle), and polymeric film formed when latex particles coalesce (right). Reprinted from [34].

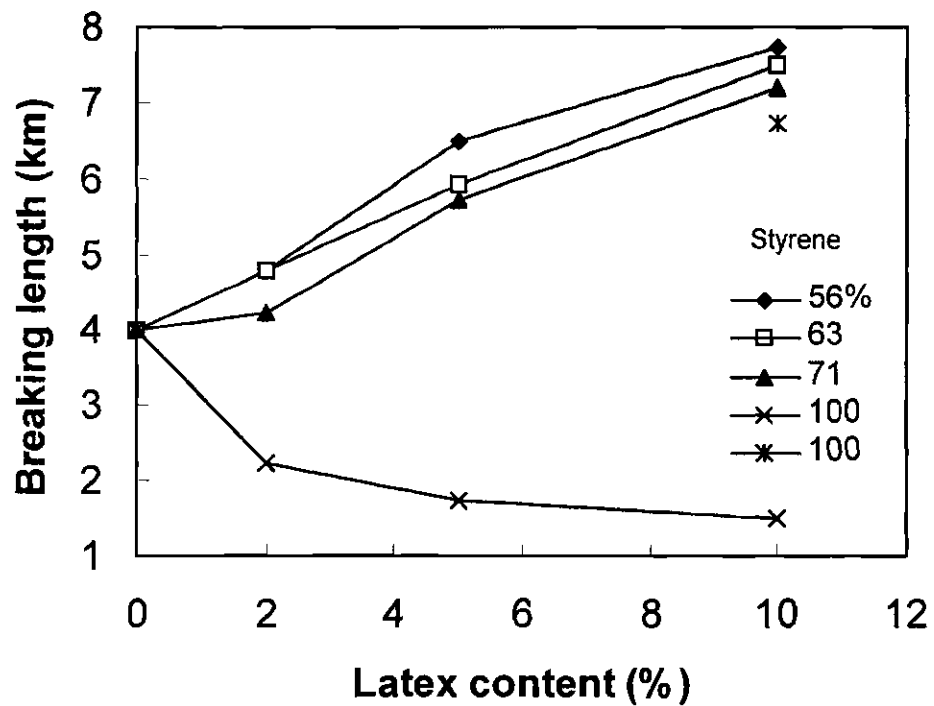


Figure 8. Improvement in tensile strength of handsheets of unbeaten, bleached kraft containing 2%, 5%, and 10% of four different latexes. Curing: 105°C, 5 hrs. Star = 150°C, 10 atm, 1 hr. Reprinted from [34].

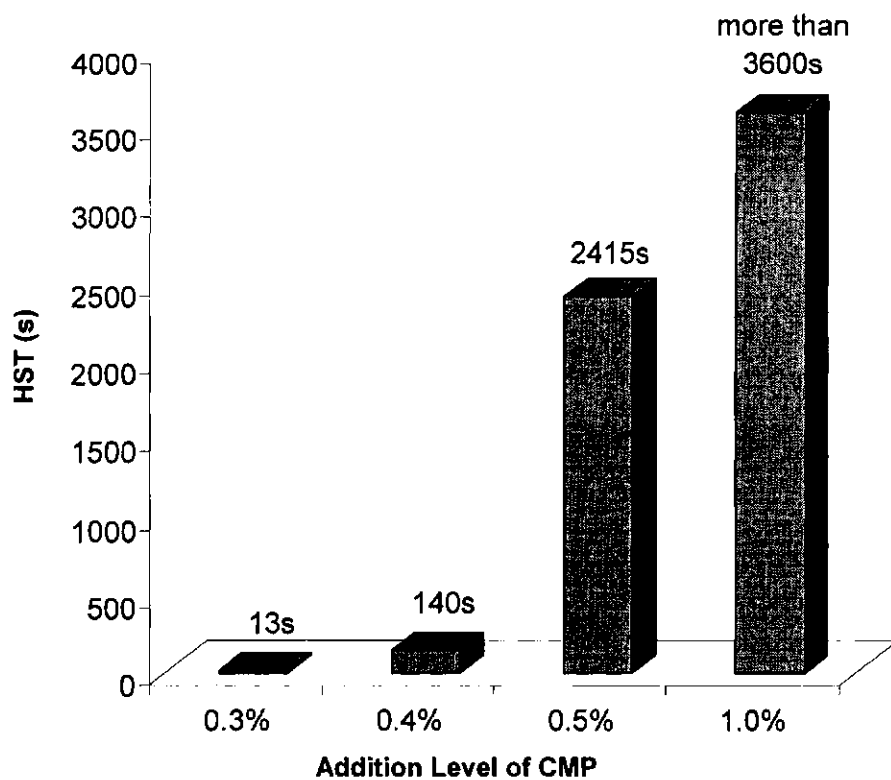


Figure 9. Sizing development with CMP. CMP: 10% cationic comonomer; curing 140°C for 30 minutes.

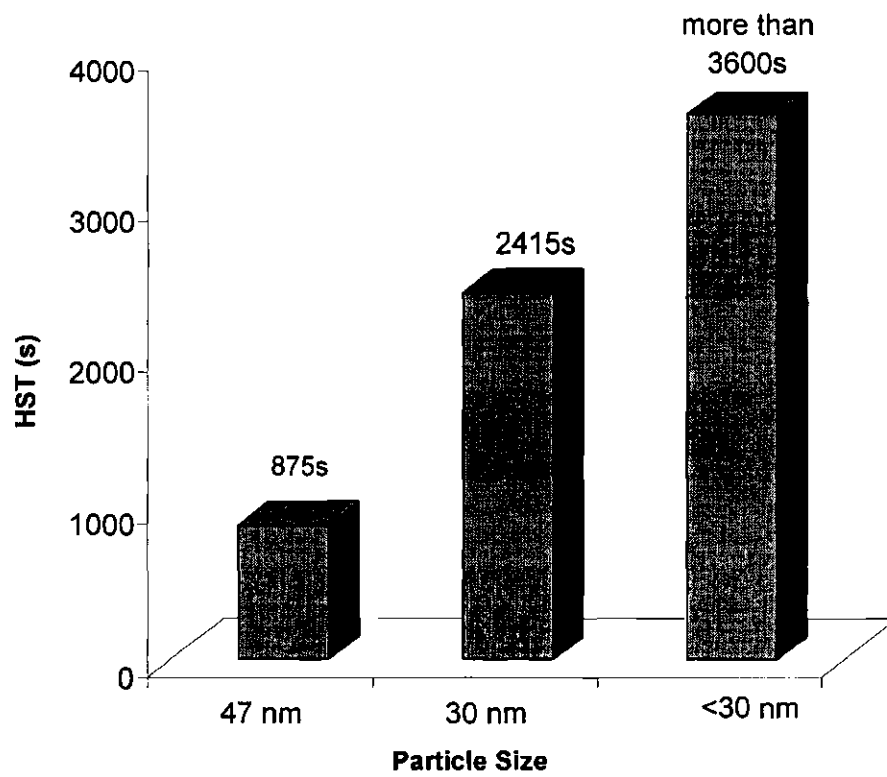


Figure 10. Effect of particle size on sizing. CMP: 10% cationic comonomer; addition level: 0.5%; curing: 140°C for 30 minutes.

Figure captions

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Table 1. Polymerization Conditions and Microparticle 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 ($\mu\text{eq}/\text{m}^2$)	-	-	2.84	3.04	3.44