Role of Cationic Polyacrylamide in Fiber-CaCO₃ Pigment Interactions

B. Alince, F. Bednar*

Pulp and Paper Research Centre, McGill University, 3420 University Street, Montreal QC H3A 2A7, Canada

ABSTRACT: It is believed that the action of cationic polyacrylamide as a retention aid for incorporating pigment particles into a paper is based on its ability to form a polymeric bridge between particles and pulp fiber suspended in water. When the polymer is added to a mixture of fibers and pigments, this process is complicated by the different rates of polymer adsorption on the fibers and the pigment particles, the rate of collision between them, and the charge reversal of the polymer from the hydrolysis. To elucidate under which conditions the polymer can form a bridge, the processes of polymer adsorption and pigment–fiber interaction were separated. A deposition of pigment particles onto fibers suspended in water was investigated, using both components pretreated with the polymer. The results indicated that polymer adsorbed on fiber can form a bridge with untreated pigment particles regardless of the polymer charge. On the other hand, negatively charged hydrolyzed polymer adsorbed on the pigment does not form a bridge with untreated fiber. When both the fiber and the pigment are pretreated, the bridge formation depends on their surface coverage by polymer and its charge. No deposition takes place when both components are sufficiently coated by anionic hydrolyzed polymer, which indicates electrosteric repulsion. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2409–2415, 2003

Key words: pigment; fiber; deposition; cationic polymer; bridge formation

INTRODUCTION

An incorporation of pigments into paper requires an effective retention of particles that are too small to be mechanically entrapped in the forming sheet. They often are also negatively charged, and consequently there is repulsion between them and the negatively charged fibers suspended in water. From this point of view the use of positively charged precipitated CaCO₃ (PCC) would present an advantage because the particles should deposit on fiber as a result of electrostatic attraction. This actually happens in distilled water.[1] However, the charge of CaCO₃ is very sensitive to any contamination because it is determined by the adsorption of cations and anions on the pigment surface.[2] Consequently, in the process water the PCC acquires a negative charge and does not deposit any more.[1] Therefore, to achieve reasonable retention, the use of a retention aid is necessary. Many products are available, the majority of them cationic polyelectrolytes that adsorb on both the fiber and the pigment. Depending on the type used, the mechanism by which

retention aids operate varies, and a number of factors affect their performance.

Highly charged cationic polyelectrolytes of moderate molar mass such as polyethylenimine act by encouraging deposition of pigment particles on fibers because of electrostatic attraction (if the two compounds become oppositely charged as a result of preferential polymer adsorption on one of them) or by charge neutralization (if the charge is eliminated by adsorbed polymer and mutual attraction as a result of van der Waals forces setting in). The process is typical of heterocoagulation, whereby the control of polymer addition is important because an excess means charge reversal of both components and consequently a repulsion between them.[1] Retention based on electrostatic attraction or charge neutralization is not very effective in a system subjected to a high shear because the tenacity of particle attachment to the fibers is not strong enough to resist particle detachment caused by hydrodynamic forces.

The second mechanism is governed by the ability of retention aids to form polymeric bridges between fibers and pigment particles. It is believed to take place when moderately charged macromolecules of high molar mass adsorb simultaneously on both components, thus keeping them together. The main representative is cationic polyacrylamide, and the process is typical of heteroflocculation. The attachment of pigment particles to fibers by a polymeric bridge is stron-
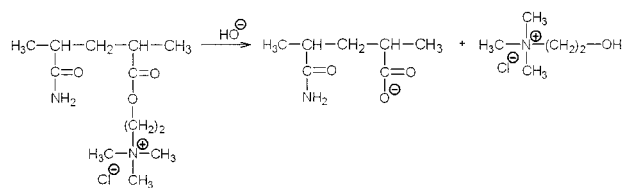
Figure 1 The expected alkaline hydrolysis of ester groups in acrylamide-based cationic copolymers. The cationic groups are converted to anionic groups very fast at a high pH. At pH 8.5 the half-life is about 15 min.[5]

ger and consequently more resistant to hydrodynamic forces.

The third mechanism is filtration, when large particles or flocs are entrapped in the forming assembly of fibers. It becomes operative when the polymer adsorbs preferentially on pigment particles, thus causing their homoflocculation and the formation of aggregates larger than the openings in the fiber web.

The bridging mechanism presents a problem. According to classical theory, for colloids flocculated by bridging there is an optimum surface coverage by polymer for maximum efficiency.[3,4] Beyond this optimum the probability of bridge formation decreases with increasing surface coverage by the polymer, and at full coverage, the particles become dispersed because of electrosteric repulsion. Therefore, it would also be expected that, at higher dosages of polyacrylamide, both fibers and pigment particles become coated, and consequently no deposition or flocculation of pigment would take place. Contrary to expectation, it has been found that PCC flocculates even with the addition of an excessive amount of cationic polyacrylamide.[5] Similarly, a deposition of pigment particles on fibers was observed when polyacrylamide was added into a mixture of fibers and pigments in such amounts that full coverage of both components could be expected.[1]

An explanation of such behavior can be sought in the different rates of polymer adsorption and particle collision.[6,7] If a bridge is formed before the adsorption of all the polymer is completed, then electrosteric stabilization may not happen. The bridge is not eliminated, even if there is an excess of polymer added. This would apply to both the homoflocculation of pigment alone and the heteroflocculation of a fiber–pigment system. In the latter, the process may be complicated further because of differences in the rate of polymer adsorption on fiber and on pigment particles. It has been shown[8] that under conditions of low shear rate polymer adsorption on fibers is a rather slow process, whereas adsorption on pigment particles proceeds at a faster rate.

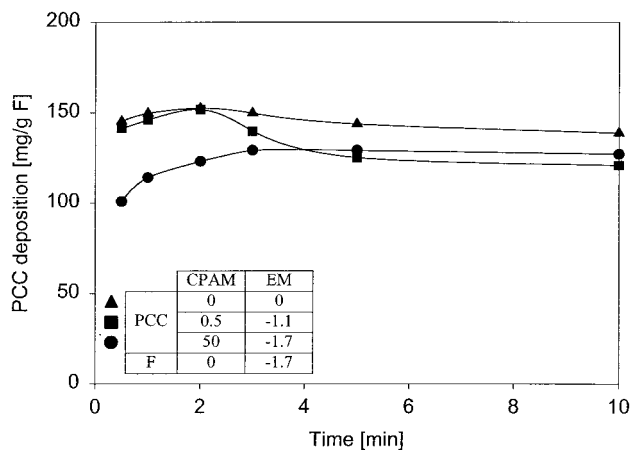To gain more information concerning the formation of the bridge between fiber and PCC, it is of interest to

Figure 2 Deposition of PCC (untreated and treated with 0.5 and 50 mg CPAM/g) on untreated fibers (F) as a function of time (inset: CPAM in mg/g, EM in 10^{-8} m^2 s^{-1} V^{-1}).

separate the process of polymer adsorption and particle deposition. Therefore, the focus of the current study was on treating fibers and pigments separately before mixing them together and observing their interaction. By adopting this procedure, other processes, such as the mixing of polymer molecules among the particles and the reconformation of adsorbed polymer toward the "equilibrium" state, are eliminated.[4]

EXPERIMENTAL

Materials

Polymer

Cationic polyacrylamide (CPAM) Percol 63 (Allied Colloids) with a 40% mole charge density and a molar mass of around 2.10^6 was used. The polymer was used as a 0.1% stock solution.
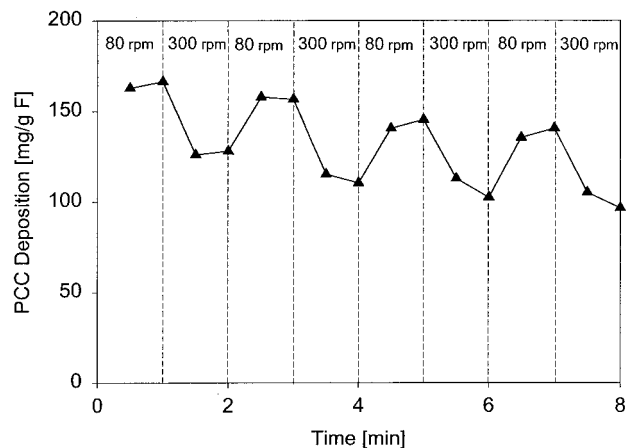

Figure 3 Deposition of untreated PCC on untreated fibers as a function of mixing speed.

CPAM	mg/g PCC	0	0.5	50
EM	10^{-8}m^{2}s^{-1}V^{-1}	0	−1.1	−1.7
Deposition	mg/g fiber	160	150	130
In sheet	mg/g fiber	36	31	42

Pigment

Precipitated calcium carbonate (PCC)—Albacar LO (Specialty Minerals)—with an average equivalent spherical diameter of 2.2 μm was used as a 1% stock dispersion. No dispersant was present. The pigment was used either untreated or treated with CPAM in amounts of 0.5 and 50 mg/g. Following CPAM adsorption on PCC dispersed in water, the supernatant was replaced by clean water in order to remove unadsorbed polymer. Regardless of the amount of CPAM used, treated PCC is negatively charged because, as a result of the high pH (around 9.5) of PCC suspension, there is fast hydrolysis of the polymer ester groups. For example, at pH 8.5 the half-time of the reaction is 15 min.[9] Thus, the positively charged amino groups of CPAM are replaced by negatively charged carboxylic groups. The expected hydrolysis reaction is shown in Figure 1.

Fibers

Softwood bleached kraft pulp was washed on an 80-mesh screen in order to remove fines. The fibers were used both untreated and treated with CPAM added in the amounts of 0.5 and 50 mg/g to fibers suspended in water at 0.2% consistency. After 30 min of mixing at pH 4 the amount of adsorbed polymer was, respectively, 0.3–0.4 and 10–15 mg CPAM/g of fiber. The data were obtained by subtracting unadsorbed polymer, which was determined in the supernatant by polyelectrolyte titration at pH 4 from the polymer added. For some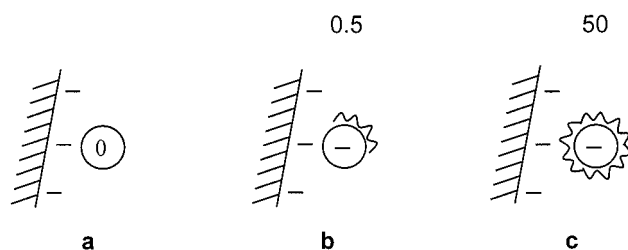 experiments the CPAM-treated fibers were exposed to pH 11 in order to hydrolyze the adsorbed CPAM and thus obtain fibers with negatively charged polymer adsorbed.

Methods

PCC deposition

One gram of fibers dispersed in 480 cm^3 of deionized water was kept suspended by slow paddle stirring (80 rpm). Following the addition of 20 cm^3 of 1% PCC (200 mg), the pH was around 9.5. The PCC deposition was determined by transmittance measurement of the supernatant at timed intervals starting at 15 s. For this, a portion of the supernatant was withdrawn using a syringe equipped with a screen to exclude fibers. From the established calibration curve of light transmittance versus concentration, the amount of PCC in the supernatant was determined. The difference between what was added and what was left in the supernatant was considered as the amount of PCC deposited on the fibers. Prior to being measured, the samples were subjected to ultrasonic treatment in order to redisperse the PCC and thus to avoid change in the calibration curve from PCC aggregation. In such a case, the calibration established for a dispersed pigment will not be valid.
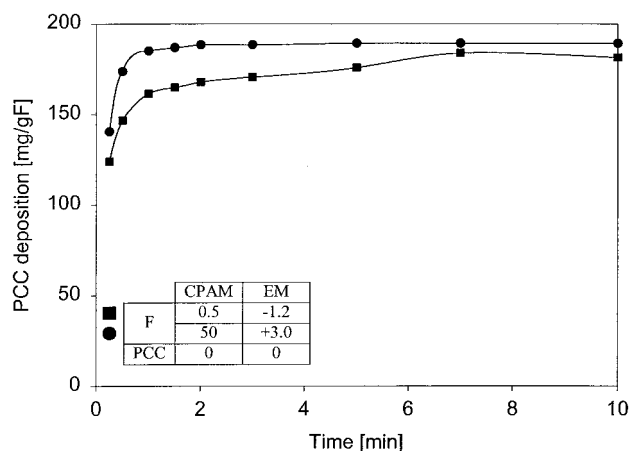

Figure 4 Schematic illustration of interaction between negative fiber and PCC: (a) untreated and uncharged; (b) treated with 0.5 CPAM/g (partly covered and negative); and (c) treated with 50 mg CPAM/g (fully covered and negative). Only van der Waals forces are responsible for PCC deposition on fibers.

Figure 5 Deposition of untreated PCC on fibers (F) treated with 0.5 and 50 mg CPAM/g as a function of time. Fibers were washed after treatment to remove unadsorbed polymers.

TABLE II
Electrophoretic Mobility (EM) of Fibers Treated with 0.5 and 50 mg CPAM/g;
Maximum Deposition of Untreated PCC (EM = 0) and Sheet Content

				Fibers hydrolyzed	
CPAM	mg/fiber	0.5	50	0.5	50
EM	$10^{-8}m^2s^{-1}V^{-1}$	−1.2	+3.0	−2.2	−2.4
Deposition	mg/fiber	180	190	195	195
In sheet	mg/fiber	115	132	149	175

At the end of the deposition experiment, the fibers were separated by forming a sheet on a 150-mesh screen in a standard sheet machine. The amount of PCC in the sheet was determined by ashing at 500°C.

Electrophoretic mobility

A microelectrophoresis apparatus, Mark II (Rank Bros., Cambridge, UK), was used. The mobility of fibers was determined on fines assumed to be representative of fibers. There are always enough fines left after their removal from the original pulp by washing to afford the measurement.

RESULTS AND DISCUSSION

PCC deposition on untreated fibers

Figure 2 shows deposition of both untreated and treated PCC as a function of time. Deposition is less than the amount added (200 mg/g of fiber), implying a dynamic equilibrium between particle deposition and detachment. The amount deposited covers only a small fraction of the fiber surface because a calculated full coverage of 1 g of fibers (about 1 m^2) by a monolayer of PCC particles (2.2 μm) would require about 2 g. Because of the lack of an energy barrier between

negatively charged fibers and untreated uncharged PCC, the driving force appears to be van der Waals attraction.

However, even in the presence of an energy barrier between fibers and negatively charged treated PCC, the extent of deposition was similar, as shown in Figure 2. There was a noticeable difference only in the slower rate of PCC treated with 50 mg CPAM/g. The apparent reason is that being dispersed because of excess polymer, the PCC deposits as single particles instead of aggregates, as is the case for both the untreated PCC and that treated with 0.5 mg/g.[5]

Deposition is also a function of hydrodynamic forces. As shown in Figure 3, by increasing the speed of mixing from 80 rpm to 300 rpm, a new equilibrium was established. The deposition is reversible, but with time a general decrease was observed.

The possibility that the polymer adsorbed on PCC may form a bridge to the fiber is not likely, as documented by a simple test. When the fibers with deposited PCC were separated by forming a sheet on a screen, the sheets contained much less pigment. The apparent reason for this was a dislocation of deposited particles being exposed to stronger hydrodynamic forces when the fibers were immobilized on the screen instead of moving with the flow. If there is a bridge, the removal of CPAM-treated
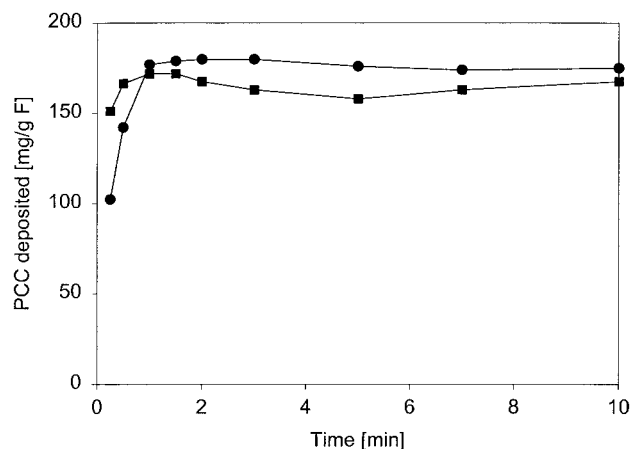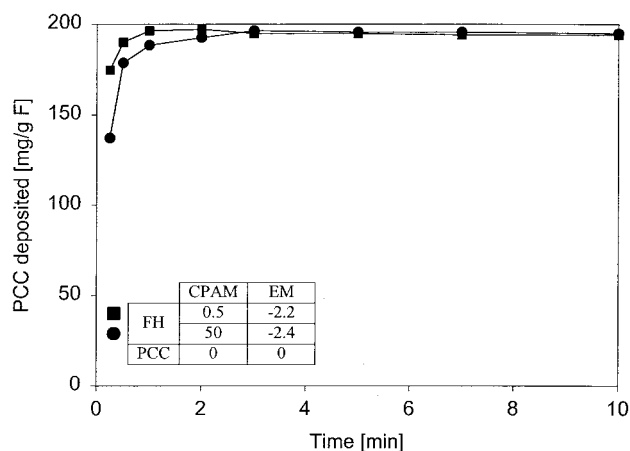
Figure 6 Deposition of untreated PCC on fibers (F) treated with 0.5 and 50 mg CPAM/g as a function of time. Fibers were not washed after treatment, and consequently unadsorbed polymer is present.

Figure 7 Deposition of untreated PCC on fibers treated with 0.5 and 50 mg of CPAM/g and hydrolyzed (FH).

PCC should be more difficult. But in all three cases the pigment content was similar, as shown in Table I, which summarizes all the relevant results: the amount of CPAM used for PCC treatment, the electrophoretic mobility of the PCC, its maximum deposition, and its content in a sheet.

The observed behavior led to the conclusion that the attractive van der Waals forces were strong enough to overcome the energy barrier arising from repulsion between the negatively charged fibers and the negative pigment particles, but no bridge was formed. The interaction between fiber and PCC is schematically illustrated in Figure 4.

Treated fibers, untreated PCC

Figure 5 shows deposition of the untreated PCC on fibers treated with 0.5 and 50 mg CPAM/g. The extent of deposition was similar in both cases, despite the negative charge of fibers treated with 0.5 mg CPAM and the positive charge of the fibers treated with 50 mg CPAM. Apparently, in the absence of an energy barrier (PCC is uncharged), the van der Waals attraction might be responsible. However, the extent of deposition was larger than that on untreated fibers, and also the content in the formed sheet was higher (compare Tables I and II). This indicates a stronger attachment of particles to fibers, most likely as a result of a polymeric bridge, in which the polymer, already adsorbed on fibers, forms a bridge by adsorbing on the colliding PCC particles.

In Figure 5, the fibers treated with polymer were washed to remove unadsorbed polymer, which may interfere with the fiber–pigment interaction. However, even if the fibers are not washed and therefore the system contains a considerable amount of free polymer (of the added 50 mg CPAM/g of fiber, only 15 mg adsorbs), the deposition, shown in Figure 6, proceeded similarly to that in Figure 5. Such behavior would indicate that a bridge between fibers and particles can form even in the presence of free CPAM because the rate of collision between the fibers and the particles is faster than the rate of polymer adsorption on the particles.

The process was complicated by the presence of PCC causing the system pH to be high (around 9–10) and due to the fast hydrolysis the CPAM adsorbed on the fibers, becoming negatively charged. To see how this charge reversal affected the bridging, the fibers with cationic polymer adsorbed were subjected to hydrolysis before the PCC was introduced. As seen in Figure 7 and Table II, the deposition on hydrolyzed fibers was even higher, indicating that anionic PAM adsorbs on PCC more effectively.[8] The compiled results on washed fibers are shown in Table II and a schematic illustration in Figure 8.
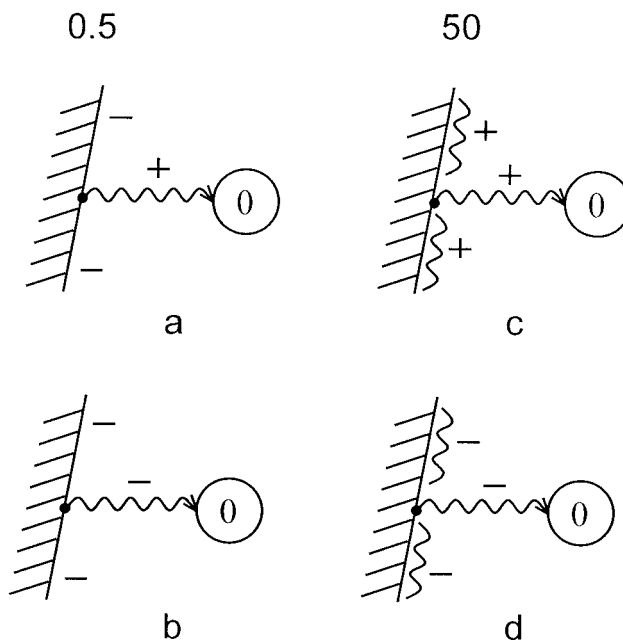

Figure 8 Schematic illustration of interaction between untreated uncharged PCC and fibers: (a) treated with 0.5 mg of CPAM/g (partly covered by positive polymer); (b) hydrolyzed (partly covered by negative polymer); (c) treated with 50 mg CPAM/g (fully covered by positive polymer); and (d) hydrolyzed (fully covered by negative polymer). Polymer adsorbed on fiber, regardless of charge, can form a bridge by adsorbing on PCC.

So far it has been established that bridging takes place when polymer adsorbed on fiber, regardless of its charge, adsorbs on PCC particles. This also happens in the presence of free (not adsorbed) polymer in the system if the collision rate between particles and fibers is faster than the rate of polymer adsorption on the particle. On the other hand, when the PCC is treated with the cationic polymer, which because of hydrolysis becomes negatively charged, no bridge is formed because the anionic polymer does not adsorb on fiber.

Treated fibers, treated PCC

In the conventional process a retention aid is introduced into the mixture of fiber and pigment. It adsorbs on both components but with a different rate depending on the collision frequency, which is a function of the number and size of particles. To eliminate this effect, both the fibers and the PCC were pretreated before being mixed together. Figure 9 shows deposition for two systems: both PCC and fibers were pretreated either with 0.5 or 50 mg CPAM/g.

In the first case the rate of deposition was fast, likely a result of the PCC being flocculated when treated with 0.5 mg CPAM/g. In the second case the PCC was dispersed because of the large amount of CPAM used
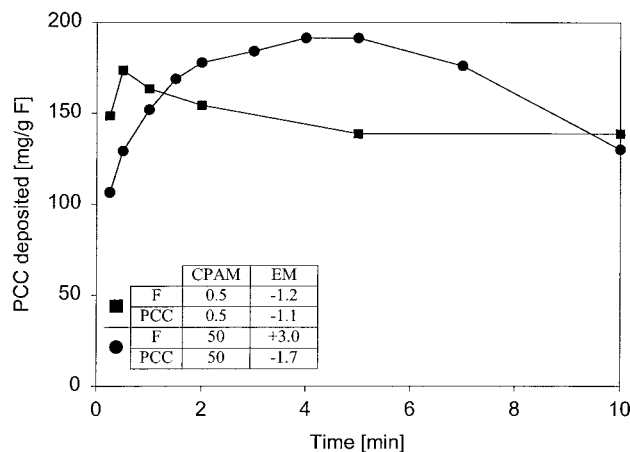
Figure 9 Deposition of treated PCC (0.5 and 50 mg CPAM/g) on treated fibers (0.5 and 50 mg CPAM/g) as a function of time. The slower rate indicates deposition of dispersed PCC particles. Departure was likely caused by gradual hydrolysis and charge reversal of the original cationic polymer.
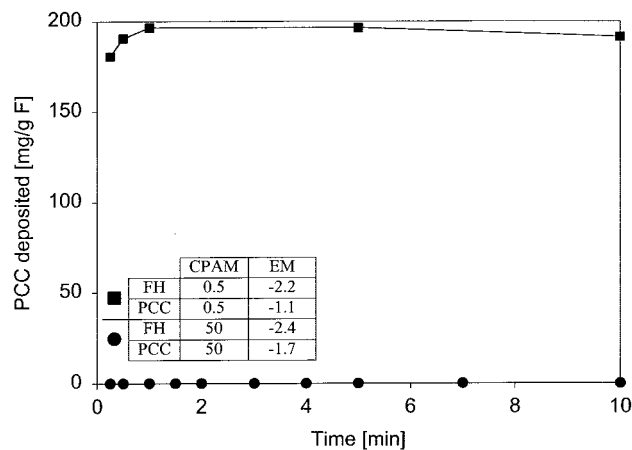

Figure 10 Deposition of treated PCC (0.5 and 50 mg of CPAM/g) on treated and hydrolyzed fibers (0.5 and 50 mg CPAM/g) as a function of time. At full coverage of both the fiber and the pigment by negative polymer, no deposition takes place.

for pretreatment, and consequently it deposited at a slower rate. In both cases, following maximum deposition, a departure of PCC was apparent. This may be because of the gradual hydrolysis and charge reversal of the originally cationic polymer adsorbed on the fibers, which took place at a high pH caused by the addition of PCC. The ensuing repulsion between the fibers becoming negative and the already deposited negative pigment may weaken their attachment and facilitate pigment removal. As a result, the PCC content in the sheet was rather low, as shown in Table III.

Figure 10 shows deposition on hydrolyzed fibers. The results are in qualitative agreement with the theoretical prediction. When 0.5 mg was used for pretreatment, only a small fraction of the PCC surface was covered, and therefore the polymer adsorbed on fiber had the opportunity to form a bridge because, regardless of its charge, it adsorbed on PCC. However, at full coverage of both the fiber and the pigment, electrosteric repulsion between them prevented any deposition. Table III shows the compiled results and Figure 11 the schematic illustration of the expected mechanism.

CONCLUSION

Deposition of untreated PCC on untreated fibers suspended in water was driven by attractive van der Waals forces. The actual amount deposited was governed by dynamic equilibrium between the rate of particle deposition on the fibers and the rate of particle departure from the fibers.

Cationic polyacrylamide preadsorbed on either the PCC or the fiber enhanced their mutual interaction if it was capable of forming a bridge. When on PCC, and because of the hydrolysis becoming negatively charged, it did not adsorb on fiber, and consequently no bridge is formed. Thus, only van der Waals forces are operative. When on fiber it adsorbed, regardless of charge, on PCC. The number of bridges, which is a function of the amount of polymer adsorbed, would determine the tenacity of attachment.

The same principle applies when both the PCC and the fibers were pretreated. Positively charged polymer on fiber adsorbed on negatively charged pretreated PCC. On the other hand, negatively charged polymer on fiber adsorbed on PCC only if the particle was not fully covered by the polymer. Therefore, when 50 mg

TABLE III
Electrophoretic Mobility (EM) of Fibers and PCC Treated with 0.5 and 50 mg CPAM/g; Maximum Deposition of Treated PCC on Treated Fibers and Sheet Content

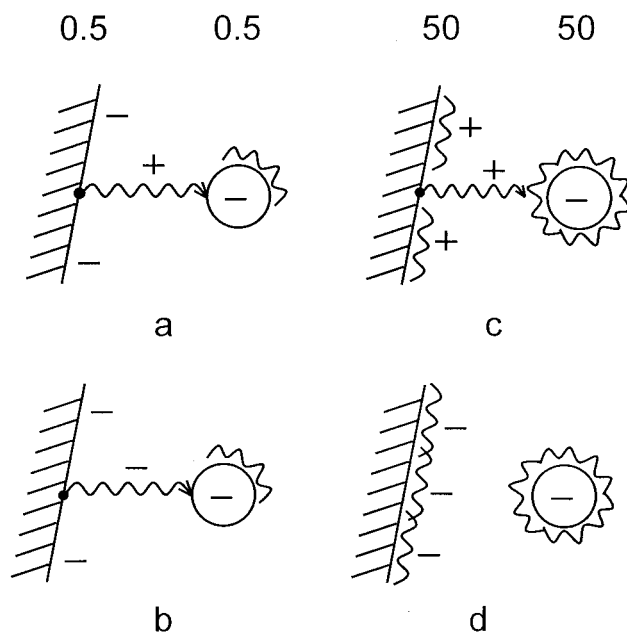|				Fibers hydrolysed	
CPAM	mg/g	0.5	50	0.5	50
EM fiber	$10^{-8} m^2 s^{-1} V^{-1}$	−1.2	+3.0	−2.2	−2.4
EM PCC	$10^{-8} m^2 s^{-1} V^{-1}$	−1.1	−1.7	−1.1	−1.7
Deposition	mg/fiber	180	190	195	0
In sheet	mg/fiber	82	94	120	0

Figure 11 Schematic illustration of interaction between PCC and fiber: (a) both treated with 0.5 mg/g CPAM (fibers partly covered by positive polymer, PCC partly covered and negative); (b) treated fibers hydrolyzed (partly covered by negative polymer); (c) both treated with 50 mg/g CPAM (fibers fully covered by positive polymer, PCC fully covered and negative); and (d) treated fibers hydrolyzed (fully covered by negative polymer). Fully coated PCC does not deposit on fully coated hydrolyzed fibers because of electrosteric repulsion.

of CPAM was used for treatment, an electrosteric repulsion between the fully coated particles and the fibers prevented any deposition. This behavior is in agreement with the theoretical prediction.

In a system where CPAM is introduced into a mixture of fiber and PCC, the formation of bridges is affected by the rate of polymer adsorption on fibers and on particles, on the rate of collision between particles and fibers, and on the rate of polymer hydrolysis. Consequently, deposition may take place even if an excess of polymer is added.

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