Flocculation Mechanism Induced by Phenolic Resin/Peo and Floc Properties

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The flocculation of an industrial furnish of TCF Kraft bleached pulp and ground calcium carbonate, induced by polyethylene oxide, and by the dual system formed by polyethylene oxide (PEO) and formaldehyde-phenol resin (PFR), was investigated and compared in order to study the flocculation kinetics, the flocculation mechanism and the properties of the formed flocs. A technique based on the measurement of the particle chord size distribution, called focused beam reflectance measurement, was used to carry out the research. The ability of the polyacrylate contained in the commercial ground calcium carbonate as a PEO cofactor was observed. Results confirmed the formation and the coacervation of the complex PFR-PEO, which loses its flocculant properties over time, confirming the complex bridging flocculation model. The shearing forces effect on the flocculation kinetics and on the properties of the formed flocs was also studied. © 2005 American Institute of Chemical Engineers *AIChE J,* 51: 1022–1031, 2005
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Introduction

Polyethylene oxide (PEO) has been used in conjunction with a cofactor as retention system in the paper industry since the mid 1980s mainly in Canada.[1–5] However, its flocculation mechanism and benefits are still controversial.

PEO is a high-molecular weight homopolymer whose general structural formula is: $(—CH_2CH_2O—)_n$. The molecular weight of the product used as flocculant is between 10^6 and 10^7 g/mol, because lower molecular weight chains do not have flocculant properties and higher ones produce polymer agglomerates. When it is dissolved, it forms a highly ordered structure with helix form whose unit cell contains seven monomeric units.[6–8] The residual polymer in the process water has the advantage of improving the flotation stage efficiency aiding the water clarification. This system is also used in water clarification and thickening processes.[9–12] This retention system can be very successful but the performance is very difficult to control and it is the subject of many research works. Since wet end stability is an important parameter in paper mills it has not been widely implemented.

The control of its efficiency is very difficult because the behavior of PEO depends on many different variables, which determine the dissolution grade of the polymer, such as the polymer molecular weight, the temperature, the shear history, the polymer solution storage time and the shearing conditions during its injection.[13–16] At room-temperature, PEO is completely soluble in water, but the dissolution process is very slow. When solid PEO is added to water, under agitation, it starts to form entanglements or nondissolved groups of many polymer chains. The agitation intensity and time disperse these entanglements and the system evolves towards an equilibrium between clusters, formed by several polymer chains, and dissolved chains. It has been demonstrated that this equilibrium is displaced towards the clusters formation as the polymer molecular weight increases.[17,18] The preparation of the solution and its age affect the proportions of clusters, molecule entanglements and dissolved molecules. Therefore, they affect the flocculant efficiency of the polymer because the clusters and entanglements behave as higher molecular weight chains.[6,13]

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The behavior of PEO as flocculant depends also on the ionic strength and the pH of the medium.[19–22]

The flocculation mechanism induced by PEO is the bridging formation between particles. PEO is able to adsorb on unbleached Kraft or sulphite fibers, latex or clay without any cofactor. The flocculant efficiency increases when the molecular weight increases and the dissolution grade decreases. It has been reported that the PEO flocculation efficiency depends on the PEO solution preparation for example the PEO concentration, the solution age, the agitation intensity and the time.[15,23]

However, PEO does not adsorb on other particle surfaces, such as calcium carbonate or bleached Kraft fibers. Therefore it is necessary to use another compound that makes possible the interaction. That compound or cofactor normally has aromatic cycles.

The polymer is able to form hydrogen bonds with other electron acceptor compounds, because of the unshared electron pairs of the ether oxygens. It has been proposed, based on this evidence, that PEO forms nonsoluble complexes with phenolic resins, polyacrylic acids and polymethacrylic acids. These are commonly used as cofactors in the dual retention systems.

The mechanism of the flocculation induced by these dual systems is still under investigation. There are several theories about the mechanism of the flocculation induced by the dual system formed by PEO and phenolic resin. The first one was established by Lindström and Glad-Nordmark, who published that the PEO and the phenolic resin formed a transitory network, which enclosed the fillers while fibers act as collectors through the network.[24,25] This theory was supported by three facts:

- The retention of the filler was significantly influenced by the particle size.
- Latex did not flocculate without fibers or if the fibers were added after the system components.
- Latex retention was increased with fiber concentration.

This theory was the most accepted until 1996 when it was observed that the efficiency of the system was very high at very low dosages, which are too low to form a network, to enclose the fillers. Furthermore, it was observed that filler retention depended on filler nature, under the same conditions: the retention of precipitated calcium carbonate was effective but the retention of ground calcium carbonate was not significant. Some authors[26,27] have proposed that the influence of the particle size on their retention is due to the increase of the van der Waals forces and the collision probability between the fiber and the fillers when the particle size increased. Another hypothesis is that in the presence of the cofactor there are more PEO entanglements and clusters than in the absence of the cofactor. Clusters could be large enough to form bridges between the particles to produce their flocculation, and this fact has been used to explain why the efficiency of the system depends on the shear history of PEO. However, this fact does not explain why the dual system is able to induce the flocculation of suspensions, which do not interact either with PEO or with phenolic resin when they are used separately.[15,26,28]

One of the most important models to explain the behavior of the dual system is the formation of association-induced bridges.[15,26] This model proposes that the cofactor interacts with the PEO forming a complex, which has lower entropy. The adsorption of the complex on the surfaces would produce a greater decrease of the Gibbs energy. This would make the adsorption stronger favoring the adsorption of the complex on surfaces where neither the PEO nor the PFR is able to adsorb, as for example, on the clean fibers surface and on the calcium carbonate particles. This theory considers also the possibility of the formation of junction points by the cofactor on the particle surfaces, when it can get adsorbed on them, which would make it possible for bridges to be formed by the PEO. Modgi et al.[29] observed that the interaction between phenolic resin and PEO is due to the hydrogen bonding between the phenolic groups and the oxygen atoms of the PEO chain, and between the aromatic cycles of the phenolic resin and the PEO chain. These hydrogen bonds would increase the stiffness of the complex and may justify why the efficient cofactors usually present aromatic cycles. Thus, it has been proposed that the complex formed by the PEO, and the cofactor forms bridges between the particles and produces their aggregation.

This theory may also explain the heteroflocculation mechanism induced by PEO, when the polymer can be adsorbed on the fillers but not on the fibers, as an asymmetric bridging flocculation. In this case the polymer could be adsorbed on the fillers and, because of that, its entropy would decrease making possible the adsorption of the filler-polymer complex on the fiber surface.[30]

Pelton's group explained the behavior of the dual system by a complex bridging model. They studied the kinetics of the main possible interactions between PEO, cofactor and latex, and they deduced that PEO and cofactor formed a complex that was adsorbed on the particles surface and produced their flocculation. This matches the association induced bridging model. However, they proposed that this complex coacervated forming a nonflocculant precipitate complex. Therefore, the flocculation process would compete with the coacervation process.[27] They also demonstrated the interaction between the cofactor and the PEO chains to form the complex.[31]

The subject of this work is to add more information in order to reach a better understanding of the flocculation induced by the dual system formed by the polyethylene oxide and the phenol-formaldehyde resin. To reach this aim we used a methodology based on a technique that measures the particle chord-size distribution. This technique is complementary to the techniques that have been used until now and it allows us to generate new data that will increase the knowledge of the behavior of the polyethylene oxide and the resin and, therefore, it will contribute to defining the flocculation mechanism.

Furthermore, this methodology allows us to optimise the flocculation induced by the dual system and to study the properties of the formed flocs. Thus, new information about the flocculation, the deflocculation and the reflocculation process will be presented.

Experimental Studies

Materials

The PEO solution was prepared as a 0.5 g/L solution of *Ucarfloc 309,* whose average-molecular weight is $8 \cdot 10^6$ g/mol in deionised water. Due to the strong effect of the shear history on the PEO behavior, the solution was prepared in the same way always stirring at 400 rpm during 60 min. The solution was prepared the day before use and it was kept at a temperature lower than 10°C until it was used. This procedure allows us to work with a homogeneous efficiency of the polymer.

• The phenol-formaldehyde resin was prepared as a 10 g/L solution of Netbond FRB in deionized water.

• The flocculation of a calcium carbonate suspension and the flocculation of an industrial pulp suspension were studied.

• The calcium carbonate suspension was a suspension of ground calcium carbonate that has 0.2% of polyacrylate as a dispersant, in deionised water, whose concentration was 10 g/L.

The pulp was prepared from a TCF Kraft pulp from eucalyptus with a consistency of 1%. 20%w on the fibers weight of ground calcium carbonate (GCC) was added to the pulp.

Method

The flocculation process was studied using laser technology, through a focused beam reflectance measurement technique (FBRM), based on the measurement of the particle chord-size distribution in real time.[32–34] This methodology was developed by the authors and was published in 1996.[35] Then it was used by other authors to study the flocculation process induced by dual systems and the stability of the formed flocs.[36,37] Finally, the methodology was completed to study the flocculation, deflocculation and reflocculation process from a kinetic point of view.[38,39] The methodology is described in detail in the references.[33]

In a typical experiment, the probe is in the stirred suspension and the flocculant is added. It is possible to add the flocculant in different steps in order to know the optimal dosage of the flocculant, also to add one dosage and observe the evolution of the flocs.

The study of the evolution of the chord size distribution was carried out by monitoring the mean chord size or the number of counts per second (the number of particles that the equipment measures each second). When the aggregation of the GCC suspension induced by the dual system was studied, the chord size distribution was bimodal after the flocculation process and the mean chord size was not the best way to represent the flocculation process. Therefore, the mean of the square weighted chord-size distribution was used because it could be a good solution for bimodality.

The floc properties were studied by adding the optimal dosage of the flocculant to the suspension stirred at 250 rpm (if it was GCC suspension) or 400 rpm (if it was pulp suspension), and after a determinate time the stirring speed was increased in order to break down the formed flocs. The high stirring intensity was maintained for 240 s and then it was reduced to the initial one in order to observe the reflocculation capability of the system. The strength, the size and the reversibility of the flocs depend on the flocculation mechanism, therefore, the study of them yields information about the flocculation mechanism of the system.

The results were analyzed using a model of the flocculation kinetics, based on the Smoluchowski model.[40,41] That model describes the kinetics of the evolution of the particle concentration (particles/L) when there are two processes that tend to the equilibrium: the flocculation process with a second-order kinetics and the formed flocs breakage with a first-order kinetics. The most similar variable we can measure by this technique is the number of counts per second, that is the number of particles whose chords the sensor has measured. This reflects the particle concentration as it evolves in the same way.

Therefore, the flocculation kinetics can be studied by using the model represented by the Eq. 1.

$$\frac{dn_c}{dt} = -k_{c1}n_c^2 + k_{c2}n_c \tag{1}$$

where n_c is the number of counts measured per second, t is the time (s), and k_{c1} and k_{c2} are functions of the Smoluchowski's kinetics constants. This allows us to compare the flocculation kinetics and the deflocculation kinetics of different trials. The relationship between both sets of kinetics allows us to obtain the equilibrium situation towards which the system tends.

During the first few seconds of the flocculation process there are not enough flocs to be destroyed. Therefore, the deflocculation process is negligible compared to the aggregation of particles. Initially, the evolution of the system can be described by Eq. 2 that results from resolving Eq. 1, without the deflocculation term

$$n_c = \frac{n_{c0}}{n_{c0}k_{c1}t + 1} \tag{2}$$

where n_{c0} is the number of counts per second before adding the flocculant.

Equation 2 allows us to obtain information about the flocculation kinetics when the behavior of the system changes a few seconds after adding the flocculant, before reaching equilibrium.

Equation 1 applied to the deflocculation process allows us to compare the floc strength in different conditions.

When there is a reflocculation process, after reducing the stirring intensity, it can be also studied by applying Eq. 1 or Eq. 2, and it is possible to compare the results with the flocculation kinetics and to obtain information about the reversibility of the flocs.

Results and Discussion

Flocculation of a GCC suspension

Initially, the flocculation induced by PEO of a suspension of GCC (1%) in distillate water was studied.

To determine the optimal PEO dosage to induce the flocculation of 200 mL of calcium carbonate suspension, the flocculant was added gradually, while the mean chord size of the particles was monitored in real time.

As Figure 1 shows, the addition of the first dosage produced an important increase in the mean chord size, although it was a very small PEO dosage, 125 mg/Kg GCC (1.25 ppm), but PEO was not supposed to interact with the calcium carbonate. This interaction could be due to the dispersant that would act as a cofactor making possible the interaction between the PEO and the particles of GCC.

Previous studies carried out with the PEO with a molecular weight of $6 \cdot 10^6$ g/mol have shown that the PEO did not affect the stability of the ground calcium carbonate in deionised water, and that it was necessary to add salt to destabilise the suspension.[42] However, Figure 1 shows that the flocculation is possible with a higher molecular weight PEO and in the absence of a cofactor. The higher molecular weight of the PEO

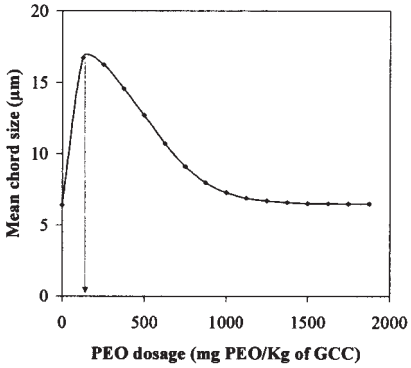

Figure 1. Evolution of the mean chord size during the gradual addition of PEO solution to a GCC suspension, of concentration 1%w. Stirring speed 250 rpm.

chains might allow them to form bridges between the particles despite the high electrical double layer thickness.

When the amount of PEO added to the suspension is higher than 1.25 ppm, the mean chord size decreased. To interpret this the chord size distributions of several dosages were compared as shown in Figure 2. The addition of 1.25 ppm produced a displacement of the distribution towards higher chord lengths indicating that the particles aggregate forming larger flocs. When the dosage of PEO is 15 ppm, the chord length distribution of the system is similar to the initial one. This indicates that the dosages of PEO higher than 1.25 ppm produce the deflocculation of the system because of the excess of polymer. Therefore, the optimal dosage is 1.25 ppm.

This optimal PEO dosage corresponds to 0.125 mg/g_{GCC}. This is a dosage 10 times lower than the optimal dosage obtained by Cechova.[42] This shows the effect of the molecular weight and the surface area on the flocculation of GCC induced by PEO. The surface area of the GCC is 2.2 m^2/g, therefore, the optimal adsorption, supposing that all the added PEO is adsorbed on the GCC particles, would be 0.057 mg/m^2. This is significantly lower than the maximum coverage reported by Cechova,[42] which was around 0.1 mg/m^2–0.3 mg/m^2. This low coverage would indicate that the flocculation mechanism is the formation of bridges between the particles. This is the most probable mechanism because the polymer is nonionic.

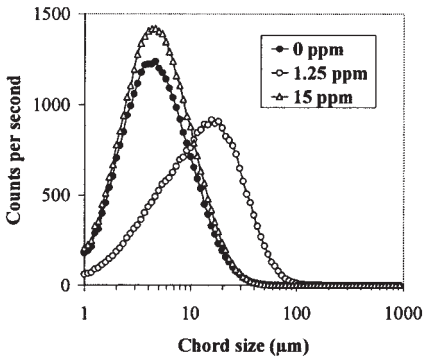

Figure 2. Chord length distributions of a 1% GCC suspension at 250 rpm when different PEO dosages were added.

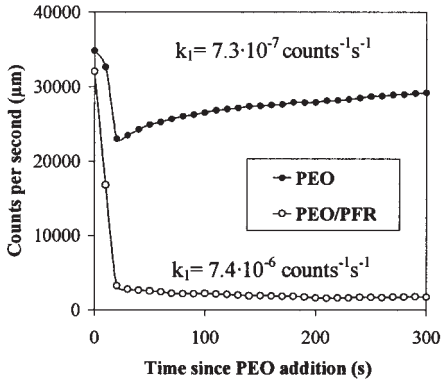

Figure 3. Effect of the PFR as a PEO cofactor.

The mean chord size starts to decrease when the PEO dosage is higher than 0.250 mg/g_{GCC}. This corresponds to a covered surface of about 0.114 mg/m^2, which is near the maximum coverage. Furthermore, the suspension is stable with a PEO dosage of 0.57 mg/m^2, which is higher than the maximum coverage. Therefore, the mean chord size decreases at high PEO dosages because of the restabilisation of the suspension due to the steric forces. This confirms that PEO interacts with the GCC but its adsorption capacity is low.

The explanation for the low adsorption capacity of PEO on GCC could be the relationship between the polyacrylate and the PEO concentrations. The commercial GCC used in this work contains a 2,000 mg/Kg GCC of polyacrylate as dispersant. Results seem to indicate that this dispersant works as a cofactor for the PEO. This could make possible the interaction between PEO and GCC, which is not the case between PEO and PCC. The optimal PEO dosage and the effect of dosages of PEO higher than 2.5 ppm indicate that the optimal ratio polyacrylate/PEO would be between 8/1 and 16/1. This means that it is necessary to have many polyacrylate molecules to form an efficient complex with one chain of PEO, assuming that the polyacrylate molecular weight is not higher than the molecular weight of PEO. It is possible that the excess PEO interacts with the polyacrylate of the complex, formed by the polyacrylate and PEO, and forms another complex with worse flocculant properties.

Furthermore, when the PEO dosage is higher the number of polyacrylate-PEO complex units could increase as well. Therefore, the coverage grade could rise and at high PEO dosages steric repulsion could be important.

As shown in Figure 3, when the optimal PEO dosage is added to the GCC suspension, the number of counts decreases because of the aggregation of the particles. After 20 s the number of counts increases in the absence of phenolformaldehyde resin (PFR). This fact indicates that some of the formed flocs without PFR are not very stable.

From a kinetic point of view, during the first seconds the flocculation process predominates and flocs are formed. When there are enough flocs deflocculation begins to be relevant and the hydrodynamic forces destroy some flocs. Then, as shown by the increase of counts (Figure 3), part of the destroyed flocs is not replaced. This might indicate that the conformation of the adsorbed PEO chains or clusters could evolve towards a flatter configuration that would not allow them to form bridges between the particles.

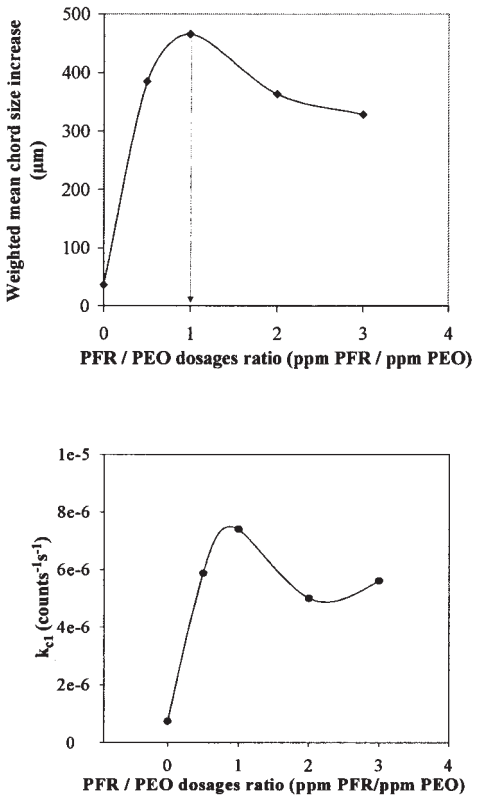

Figure 4. Determination of the optimal relationship between the PFR and the PEO dosages. Dosage of PEO = 1.25 ppm.

The results presented in Figure 3, were obtained by adding 1.25 ppm of PEO to the GCC suspension, or by adding 1.25 ppm of PFR first, and after 60 s the same dosage of PEO. These show that the utilization of PFR as a cofactor improves the flocculation rate and the stability of the flocs as it increases the value of the k_{c1} constant by 10 times and forms more stable flocs. This demonstrates the important role of this compound in the flocculation mechanism.

The optimal relationship was determined by carrying out the flocculation of the GCC suspension, induced by different dosages of PFR and the same dosage of PEO that is 1.25 ppm, as shown in Figure 4. The optimal relationship was 1:1 because it produced the fastest flocculation and the largest flocs.

It was also necessary to optimise the dual system dosage with the optimal relationship between the dosages of both components of the dual system. Because of that the flocculation of the GCC suspension was carried out by adding different dosages of both polymers with a dosage ratio of 1:1, in order to get the optimal dosage of PFR and PEO. Figure 5 shows that the optimal dosage is 2.5 ppm, which again produces the fastest flocculation and the largest flocs. This optimal dosage is double the optimal dosage of PEO obtained from Figure 1.

Big flocs are formed at polymer dosages of 2500 mg/Kg_{GCC}, that corresponds to a coverage of 1.14 mg/m^2. However, GCC flocculation induced by PEO, without adding the cofactor, was negligible at dosages higher than 1,000 mg/Kg_{GCC} (see figure 1). Furthermore, this coverage is high enough to produce steric repulsion and stabilize the suspension.

Figure 5 shows that an excess of both polymers decreases the flocculation rate because some particles, which were near the polymer addition point, could have too much adsorbed complex and they might suffer steric repulsion. They could then not aggregate until finding other particles with low coverage.

These facts show that the PFR improves the adsorption capacity of PEO on GCC and the flocculation process. The reason for this could be that PFR and PEO form a complex, and when this complex is adsorbed on GCC its conformation is more extended than the conformation of the adsorbed polyacrylate-PEO complex.

In order to study the role of the PFR in the flocculation of GCC suspension induced by the dual system, trials were carried out in the optimal conditions by adding both components of the dual system at the same time to the suspension.

As figures 6 and 7 show, there is no difference between the obtained results and the evolution of the flocculation process when it was carried out by adding the PFR 60 s before the PEO addition. This demonstrates that the PFR does not need to adsorb on the particles before flocculation takes place. It does not form junction points on the particles surface to make possible the PEO adsorption, but it interacts with the PEO in the solution and forms a complex that adsorbs on the particles. This confirms the theories of association induced bridging and the complex bridging flocculation.

Figures 6 and 7 also show that the complex evolves and loses the flocculant properties quickly. When the components of the dual system were mixed together 5 or 15 s before adding them to the suspension, the flocculation rate decreases and the de-

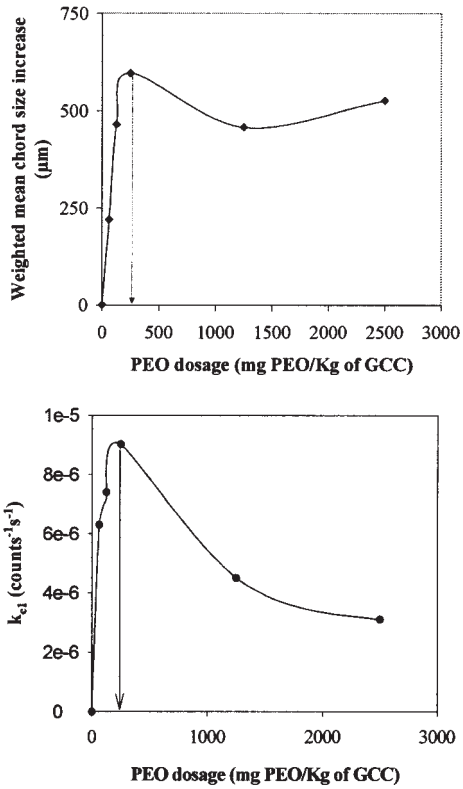

Figure 5. Optimal dual system dosage determination from a kinetic point of view. PFR/PEO = 1/1.

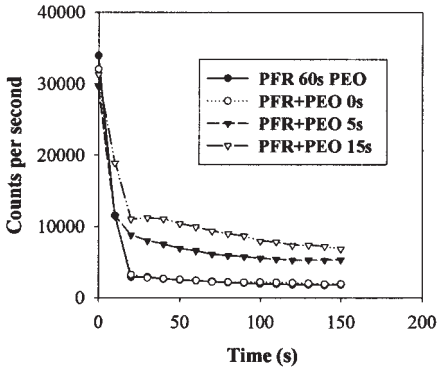

Figure 6. Role of PFR in the flocculation mechanism.

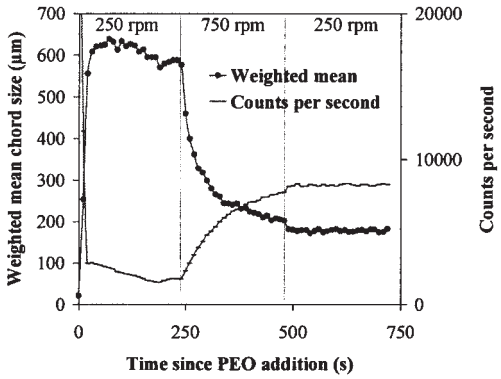

Figure 8. Properties of the flocs formed by GCC flocculation induced by the dual system.

flocculation rate increases, as shown in Figure 7. This indicates that there are less complex units that are able to form bridges between the particles (therefore, the collision efficiency is lower and the flocculation kinetics is slower). Furthermore, the higher k_{c2} values show the low stability of the formed flocs, indicating that many of the formed bridges are weaker. Therefore, the flocculant efficiency of the complex decreases when it is allowed to evolve. These results would confirm the coacervation of the complex predicted by the complex bridging flocculation model. This process and the flocculation process would compete as both have similar time scales.

Figure 8 shows the evolution of the particle size (represented by the mean chord size of the square weighted chord size distribution), and the evolution of the number of counts during the flocculation of the GCC suspension. It also shows the breakage of the formed flocs produced by increasing the stirring intensity and the reflocculation process, when the stirring intensity is reduced again.

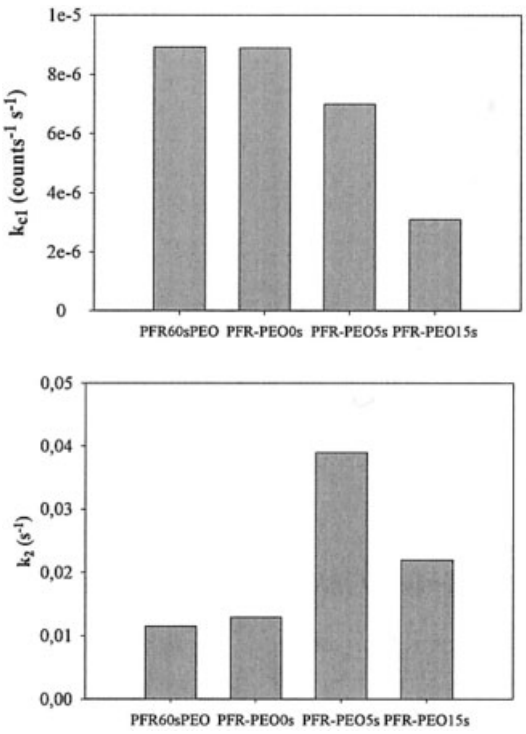

Figure 7. Role of PFR in the flocculation mechanism.

When the PFR and the PEO were added to the GCC suspension and stirred at 250 rpm, stable flocs were formed. Then the stirring intensity was increased to 750 rpm, and many of these flocs were destroyed because of the hydrodynamic forces. After 4 min the stirring intensity was reduced to the initial level and this made possible the reflocculation of the system. However, the particles did not aggregate, again showing that the flocs were irreversible. Table 1 explains this fact from a kinetic point of view. During the deflocculation process the flocculation rate decreases to a third, that indicates that the flocculant efficiency of the complex is lower than it was before. Then, after breaking the particles, the complex can evolve and it can lose its flocculant properties. Furthermore, the floc strength is lower because of the stronger hydrodynamic forces, as shown by the higher deflocculation rate (higher k_{c2} value), and the result is the destruction of the flocs. When the flocs were destroyed, at 750 rpm, the PFR-PEO complex could evolve towards a form without flocculant properties and when the stirring intensity decreased again, the particles could not aggregate because the complex had evolved to a non flocculant form. Therefore, the irreversibility of the formed flocs would confirm the coacervation of the free complex and the flattening of the adsorbed complex.

When the stirring intensity decreased to 250 rpm, the number of counts increased slightly and the weighted mean chord size diminishes slightly. This indicates that a little deflocculation is produced after decreasing the stirring. The explanation of this behavior could be the difference of collision frequencies at 250 rpm and 750 rpm. At 750 rpm, the flocs are broken and they form particles. These particles can collide again before the evolution of the complex and form a floc. When the stirring intensity decreases to 250 rpm, this possibility decreases too, because the collision frequency decreases.

Table 1. Flocculation and Deflocculation Kinetics for GCC Suspension

	Flocculation	Deflocculation
k_{c1} (counts^{-1} s^{-1})	$8.6 \cdot 10^{-6}$	$2.9 \cdot 10^{-6}$
k_{c2} (s^{-1})	$1.3 \cdot 10^{-2}$	$2.6 \cdot 10^{-2}$

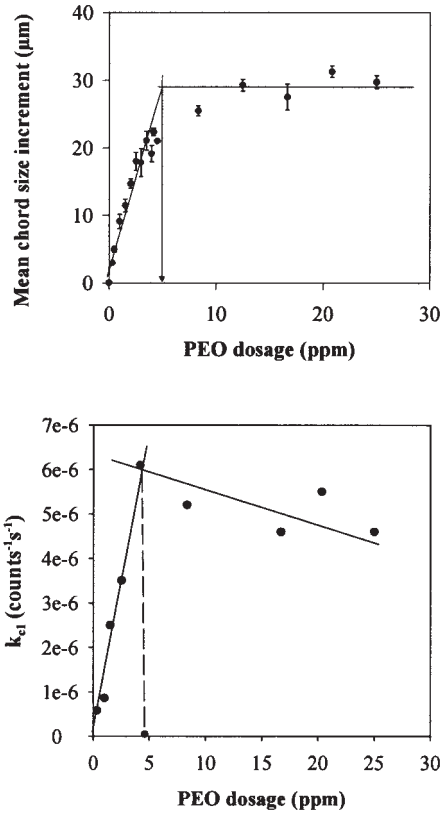

Figure 9. Determination of the optimal dosage of the dual system: ratio PFR: PEO = 1:1.

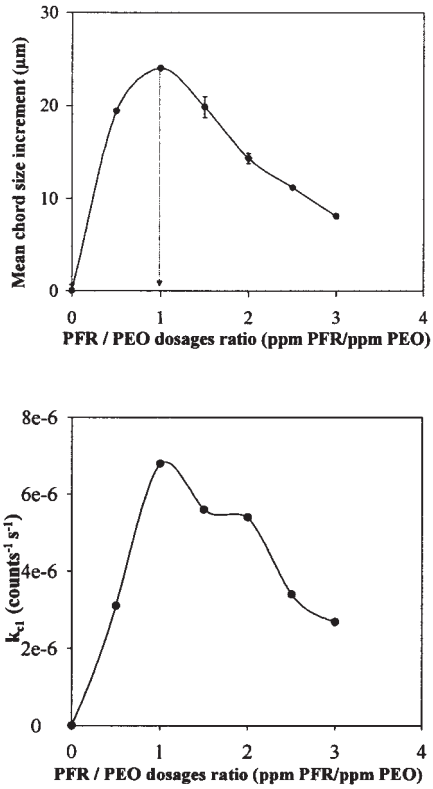

Figure 10. Determination of the optimal relationship between the dosages of PFR and PEO. Dosage of PEO = 5 ppm.

Flocculation of a pulp suspension

When different PEO dosages were added to the pulp suspension there was no significant flocculation process, despite the presence of GCC. This result shows that the PEO does not interact with the fibers without the presence of FPR. The optimal relationship between the dosage of PFR and the dosage of PEO for the GCC suspension is 1:1, as shown in figure 4. Therefore, the optimal dosage for the pulp suspension was determined by trials carried out with a ratio between the PFR and the PEO dosage of 1:1 and different dosages of the dual system. Furthermore, most of the investigations on the pulp flocculation induced by the dual system have been carried out by using 1:1 relationship between both component dosages.[15,24,25,29,43,44]

Figure 9 shows the increment of the mean chord size, obtained when the dual system was added to 300 mL of pulp suspension stirred at 400 rpm. At low polymer dosages, the mean chord size and the flocculation rate increases with the dosage of the dual system. However, polymer dosages higher than the optimal do not produce larger flocs and decrease the flocculation rate, as shown in Figure 9. Therefore, the optimal dosage of the dual system is around 5 ppm.

With this dosage, it is possible to determine the optimal ratio between the PFR and PEO dosages. Figure 10 shows the obtained results when the dual system was added to 300 mL of pulp suspension stirred at 400 rpm, with different relationships between both components of the system. It shows that the optimal dosage ratio is 1:1. It corresponds to the maximum flocculation rate and produces the largest flocs.

The PFR dosages that are higher than the optimal one affect the flocculant kinetics and the floc size. It could be because an excess of PFR remains in the solution and acts as a dispersant for the suspension. To study this hypothesis 15 ppm of PFR were added to the pulp suspension, and the behavior of the system was monitored during the first 60 s. Figure 11 shows that the chord-size distribution and the number of counts per second did not change after adding the PFR solution. Therefore, the PFR does not act as a dispersant of the pulp suspension.

To explain the negative effect of an excess of PFR on the flocculation process we must assume that most of the PFR joins

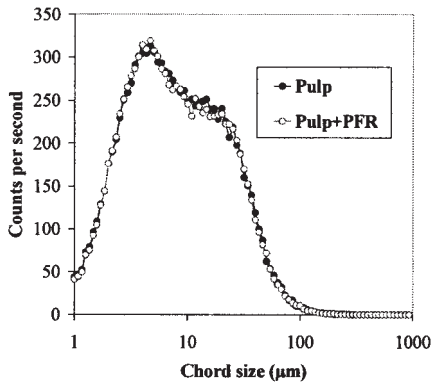

Figure 11. Effect of the PFR on the pulp suspension.

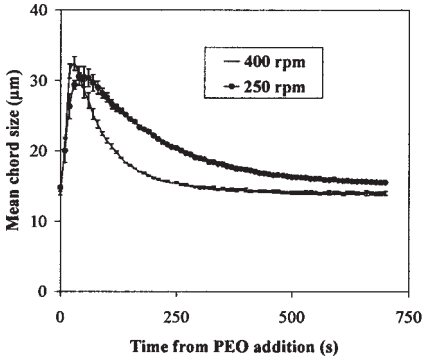

Figure 12. Effect of the stirring intensity on the flocculation process and floc stability.

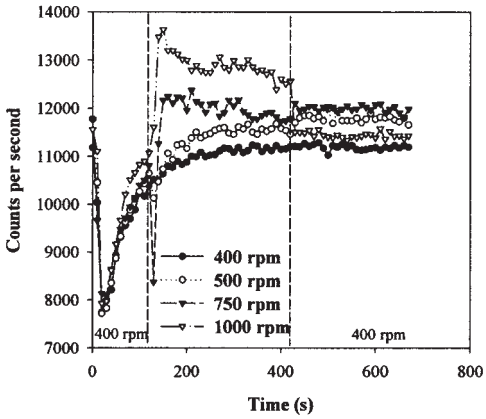

Figure 13. Mean chord size evolution during the flocculation-deflocculation-reflocculation of a pulp suspension induced by the dual system PEO/PFR.

to the PEO chains and forms a complex. Therefore, there would be more junction points between PEO chains and because of that the complex could be less extended than the complex formed when the dosage ratio of both components is 1:1. This would decrease the flocculant efficiency.

In the optimal conditions, the flocculation of the pulp induced by the dual system produced unstable flocs. As is shown in Figure 12, these flocs were destroyed to reach almost the initial state of the pulp. This phenomenon could be explained by taking two processes into consideration at the same time for example, the aggregation of particles and the destruction of some of the formed flocs.[40] During the first seconds after adding the flocculant there are not enough flocs, therefore, the particles aggregation predominates. After that time, some of the formed flocs are destroyed by the hydrodynamic forces and then there are two different possibilities:

(1) the resulting particles, which have the complex on their surfaces, could collide again immediately, before the complex evolves and then they form another floc, or

(2) the complex might evolve losing its flocculant properties before the particles collide with others and then the collision is not successful.

Therefore, some of the destroyed flocs are not formed again. After 30 s, the floc concentration starts decreasing because of this fact. The flocculation rate and the deflocculation rate were studied and Table 2 summarises the results.

Table 2 shows that the increase in the stirring intensity improves the flocculation rate during the initial stage (first 30 s) and during the evolution of the system. However, the hydrodynamic forces are higher at 400 rpm and, because of this, the deflocculation rate is also increased. Consequently, the formed flocs at 400 rpm are destroyed faster than the flocs formed at 250 rpm.

With all these considerations it is possible to explain the behavior of the system by increasing the stirring intensity, after carrying out the initial flocculation at 400 rpm and, after 5 minutes, decreasing the stirring intensity again, as shown in Figure 13.

Two minutes after the flocculant addition, the stirring intensity was increased when there were some flocs already present in the suspension. During the first 10 s, when the stirring intensity increased from 400 rpm to 500 rpm or 750 rpm, particles aggregated again. This could be because of the increase in collision frequency. Table 3 shows that the flocculation rate increases by almost two times when the stirring intensity increases to 500 rpm. Because there are not many flocs, flocculation is the predominant process during this time. After these 10 s, the deflocculation rate increases too and, being the predominant process, the system is completely dispersed again. At 1,000 rpm the system reached a more dispersed situation than the initial one.

At 750 rpm the suspension state almost reached the most flocculated situation. As was shown by figure 7, the flocculant efficiency of the PFR-PEO complex should be very low when the system has evolved during 150 s. However, the increase of the hydrodynamic forces can flocculate the system for a few seconds. This fact indicates that perhaps, at 750 rpm, the hydrodynamic forces are strong enough to break part of the PFR coacervated complex and some flocculation could be possible again.

When the stirring intensity decreased to 400 rpm, the system evolved towards the initial situation, before the flocculant was added. Therefore, there was no reflocculation process. The pulp flocculation induced by the PFR-PEO dual system formed irreversible flocs.

Conclusions

(1) In this article a kinetic model, based on the theory of Smoluchowski, has been successfully used to study the floc-

Table 2. Flocculation and Evolution Kinetics

	Flocculation		Evolution of Flocs	
	250 rpm	400 rpm	250 rpm	400 rpm
k_{c1} (counts^{-1} s^{-1})	$2.2 \cdot 10^{-6}$	$6.8 \cdot 10^{-6}$	$6 \cdot 10^{-7}$	$1.2 \cdot 10^{-6}$
k_{c2} (s^{-1})	—	—	$7.3 \cdot 10^{-3}$	$1.3 \cdot 10^{-2}$

Table 3. Pulp Flocculation and Deflocculation Kinetics after Increasing the Stirring Intensity

	400 rpm	500 rpm	750 rpm
k_{c1} (counts^{-1} s^{-1})	$1.2 \cdot 10^{-6}$	$2.3 \cdot 10^{-6}$	$3.6 \cdot 10^{-6}$
k_{c2} (s^{-1})	$1.3 \cdot 10^{-2}$	$2.7 \cdot 10^{-2}$	—

culation kinetics and the floc properties from the evolution of the chord-size distribution.

(2) With the obtained results it is possible to propose the complex bridging flocculation as the mechanism of aggregation induced by the dual system, formed by formaldehyde phenolic resin and polyethylene oxide.

(3) The PFR-PEO complex for some time decreased the flocculation rate of the suspension as well as the floc strength. There is a competition between the coacervation of the complex and the particle aggregation.

(4) The dispersant contained in the GCC slurries acts as cofactor, and it makes possible the flocculation of GCC without adding any cofactor.

(5) The flocculation of the eucalyptus TCF Kraft bleached pulp was not possible without the cofactor, despite the presence of GCC and, consequently, of the GCC dispersant (polyacrylate). The optimal relationship between the dosage of the PFR and PEO, from the point of view of pulp flocculation, was 1:1. The excess PFR, in respect to this ratio, does not disperse the fibers in the pulp suspension despite its anionic charge, but it forms part of a less extended PFR-PEO complex with worse flocculant properties.

(6) High shearing forces could destroy the coacervate and could recover the flocculant efficient form of the PFR-PEO complex. Therefore, it can produce a fast flocculation of the suspension forming unstable flocs.

Literature Cited

1. Pelton R, Allen LH, Nugent HM. A survey of potential retention aids for newsprint manufacture. *Pulp Pap. Canada.* 1980;81(1):54-62.
2. Pelton R, Allen LH, Nugent HM. *Additives for Increased Retention and Pitch Control in Paper Manufacture.* US4313790, 1982.
3. Chin-Hua T. *Method for Improving the Retention of Fines in Papermaking using Polyethylene Oxide.* CA1137261, 1982.
4. Xu Y, Deng Y. Retention of precipitated calcium carbonate in old corrugated container furnishes. *Tappi J.* 1999;82(8):121-126.
5. Trigylidas D, Englezos P, Thorburn L. The use of a fixative in conjunction with poly(etilene oxide) for enhanced retention. *Tappi J.* 2001;84(7):53. Available from: http://www.tappi.org.
6. Braun BD, Delong DJ. Polyethers (ethylene oxide polymers). In: Mark HF, Othmer DF, Overberger CG, Seaborg GT, eds. *Kirk-Othmer, Encyclopedia of Chemical Technology,* 3rd ed. New York: Wiley, 1982:616-632.
7. Davidson RL. *Handbook of Water-Soluble Gums and Resins,* New York: McGraw-Hill, 1980.
8. Stone FW, Stratta JJ. Ethylene oxide polymers. In: Mark HF, Bikales NM, Overberger CG, Menges B, Kroschitz JL, eds. *Encyclopedia of Polymer Science and Technology.* New York: Wiley, 1986:103-145.
9. Beaudoin R, Dubé G, Lupien B, Lauzon E, Vines M, Blais S. Increased retention and drainage and controlling stickies deposition with bentonite in combination with polyethyleneoxide and cofactor—a mill experience. *84th Annual Meeting, Technical Section CPPA.* Montreal, Canada, 1998:293-297.
10. Polverary M, Allen LH, Sithole B. Effect of system closure on retention and drainage aid performance in TMP newsprint manufacture. Part I. *Tappi J.* 1999;82(4):188-195.
11. Polverari M, Allen LH, Sithole B, Gagnon P, Samuel JF. The effect of converting from 100% OCC to 50% OCC: 50% NSSC on retention and drainage in a closed-cycle paperboard mill. *Tappi J.* 2001;81(1): 99. Available from: http://www.tappi.org.
12. Polverari M, Allen LH, Sithole B. Effect of system closure on retention and drainage aid performance in TMP newsprint manufacture, Part II. *Tappi J.* 2001;84(3):56. Available from http://www.tappi.org.
13. Brine SR, Brauer RM, Wiseman N. Polyethylene oxide makedown procedures and their effect on paper machine retention. *Appita J.* 1992;45(2):118-120.
14. Gibbs A, Pelton R. Effect of PEO molecular weight on the flocculation and resultant floc properties of polymer-induced PCC flocs. *J. Pulp Paper Sci.* 1999;25(7):267-271.
15. Van de Ven TGM, Qasaimeh MA, Paris J. PEO induced flocculation of fines: effects of PEO dissolution conditions and shear history. In: *Proc. of 2003 Int. Paper and Coating Chemistry Symp.* Montreal, Canada: PAPTAC, PAPRICAN, 2003:53-57.
16. Bednar F, Périn-Levasseur Z, van de Ven TGM, Paris J. Polyethylene oxide disentanglement. *J. Pulp Paper Sci.* 2004;30(2):49-52.
17. Bailey FE, Koleske JV. Configuration and hydrodynamic properties of the polyoxoethylene chain in solution. In: Schick MJ, eds. *Nonionic Surfactants Physical Chemistry.* Santa Bárbara, California: Marcel Dekker Inc., 1987:928-969.
18. Polverary M, van de Ven TGM. Dilute aqueous poly(ethylene oxide) solutions: clusters and single molecules in thermodynamic equilibrium. *J. Phys. Chem.* 1996;100(32):13687-13695.
19. Khoultchaev KH, Pang P, Kerekes RJ, Englezos P. The role of poly(ethylene oxide)-water solution phase behaviour in the retention of fibre fines and clay. *Can. J. Chem. Eng.* 1997;75(2):161-166.
20. Khoultchaev KH, Pang P, Kerekes RJ, Englezos P. Temperature-dependent behaviour of polyethylene oxide in papermaking suspensions. *AIChE J.* 1997;43(9):2353-2358.
21. Pang P, Englezos P. Phase separation of PEO-water solution and its relationship to the flocculating capability of the PEO. *Fluid Phase Equilibr.* 2001;194:1059-1066.
22. Bailey FE, Callard RW. Some properties of poly(ethylene oxide) in aqueous solution. *J Appl Polym Sci.* 1959;1(1):56-62.
23. Kratochvil D, Alince B, van de Ven TGM. Flocculation of clay particles with poorly and well dissolved polyethylene oxide. *J. Pulp Pap. Sci.* 1999;25(9):J331-J335.
24. Lindström T, Glad-Nordmark G. Selective adsorption, flocculation and fractionation of wood pulps with polyethyleneoxide. *J Colloid Interf Sci.* 1983;94(2):404-411.
25. Lindström T, Glad-Nordmark G. Network Flocculation and fractionation of latex particles by means of a polyethyleneoxide-phenolformaldehyde resin complex. *J Colloid Interf Sci.* 1984;97(1):62-67.
26. Van de Ven TGM, Alince B. Association-induced polymer bridging: new insights into the retention of fillers with PEO. *J Pulp Pap. Sci.* 1996;22(7):J257-J263.
27. Xiao H, Pelton R, Hamielec A. Retention mechanisms for two component systems based on phenolic resins and PEO or new PEO-copolymer retention aids. *J Pulp Pap Sci.* 1996;22(12):J475-J485.
28. Carignan A, Garnier G, van de Ven TGM. The flocculation of fines by PEO/cofactor retention aid systems. *J Pulp Paper Sci.* 1998;24(3):J94-J98.
29. Modgi SB, Trigylidas D, Thorburn I, Englezos P. Different trends in retention of calcium carbonate and clay in mechanical pulps with PEO/cofactor/coagulant and the role of the hydrogen bonding interactions. In: *Proc of 2003 Int Paper and Coating Chemistry Symp.* Montreal, Canada: PAPTAC, PAPRICAN, 2003:7-17.
30. Alince B, van de Ven TGM. Effect of polyethylene oxide and kraft lignin on the stability of clay and its deposition on fibers. *Tappi J.* 1997;80(8):181-186.
31. Lu C, Cong R, Pelton R. The PEO/cofactor interaction-model studies. In: *Proc. of 2003 Int. Paper and Coating Chemistry Symp.* Montreal, Canada: PAPTAC, PAPRICAN, 2003;51-52.
32. Preikschat FK, Preikschat E. *Apparatus and Method for Particle Analysis.* US5012118; 1989.
33. Blanco A, Fuente E, Negro C, Tijero J. Flocculation monitoring: focused beam reflectance measurement as a measurement tool. *Can J Chem Eng.* 2002;80(4):734-740.
34. Hokanson JV, Reed BW. *Apparatus and Method for Particle Analysis.* US5426501, 1995.
35. Blanco A, Negro C, Hooimeijer A, Tijero J. Polymer optimization in paper mills by means of a particle size analyzer: an alternative to zeta potential measurements. *Appita J.* 1996;49:113-116.
36. Alfano CJ, Carter WP, Gerli A. Characterization of the flocculation dynamics in a papermaking system by non-imaging reflectance scanning laser microscopy. *Nordic Pulp Pap Res J.* 1998;13:159-165.
37. Alfano CJ, Carter WP, Whitten JE. Use of scanning laser microscopy to investigate microparticle flocculation performance. *J Pulp Paper Sci.* 1999;25:189-195.
38. Blanco A, Negro C, Fuente E, Tijero J. Study of filler flocculation mechanisms and floc properties. In: *Proc. of 2003 Int. Paper and*

Coating Chemistry Symp. Montreal, Canada: PAPTAC, PAPRICAN, 2003;141-144.
39. Fuente E, Blanco A, Negro C, San Pio I, Tijero J. Monitoring flocculation of fillers in papermaking. *Paper Technol.* 2003;44(8):41-50.
40. Van de Ven TGM. *Colloidal Hydrodynamics* 1st ed. Padstow: Academic Press, 1989.
41. Thomas DN, Judd SJ, Fawcett N. Flocculation modeling: a review. *Water Res.* 1999;33(7):1579-1592.
42. Cechova M, Alince B, van de Ven TGM. Stability of ground and precipitated $CaCO_3$ suspensions in the presence of polyethylene oxide and kraft lignin. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 1998;141:153.
43. Xiao H, Gibbons S, Oveden C, Wiseman N. Clay retention induced by poly(ethylene oxide) with various cofactors. *Appita J.* 1999;52(2):114-120.
44. Van de Ven TGM. Mechanisms of fines and filler retention with PEO/cofactor dual retention aid systems. *J Pulp Pap Sci.* 1997;23(9): J447-J451.

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