

# **Polymeric branched flocculants effect on flocculation process of pulp suspensions in papermaking industry.**

**Ángeles Blanco, Elena Fuente, Noelia Cortés, Carlos Negro\*.**

*Chemical Engineering Department, Chemistry Faculty, Complutense University of Madrid, Avda.*

*Complutense s/n. 28040 Madrid. Spain. [cnegro@quim.ucm.es](mailto:cnegro@quim.ucm.es)*

## **Abstract**

This paper presents the effect of the structure of cationic polyacrylamides (CPAMs) on flocculation of pulp suspensions and floc properties. A focused beam reflectance measurement (FBRM) probe was used to monitor flocculation, deflocculation and reflocculation processes on real time. To carry out the study, 1% ECF eucalyptus kraft pulp containing 20% of ground calcium carbonate (GCC) was used.

Results show that the effect of CPAMs structure depends on charge density and polymer dose. Floc size not always decreases with branching degree, whereas floc stability and reflocculation ability increased when highly charged and branched CPAM was used. These findings indicate that the use of highly branched CPAMs with very high molecular weight is very promising as retention aids to improve the papermaking process.

## 1. Introduction

Flocculation is a key issue in papermaking. The use of flocculants in papermaking is required to retain fillers and additives in the fibre network, which otherwise would be lost or accumulated in the white waters. During the last years, the effect of flocculant characteristics on flocculation and floc properties have been widely studied in order to improve the productivity of papermaking process and the quality of final product by means of the optimization of retention, drainage and sheet formation<sup>1-5</sup>.

Nowadays, polyacrylamides (PAMs) are one of the most frequently used flocculants. Most of PAMs used as flocculants consist of polymers made by the combination of acrylamide monomer with other kinds of monomers as, for example, acrylates. Flocculation efficiency induced by PAMs depends on its structure, molecular weight and charge density. These properties can be modified depending on the monomers nature and proportions. Consequently, a wide variety of PAMs can be synthesised<sup>6-8</sup>. The effect of molecular weight, charge density and chemical properties of PAMs on flocculation is well known<sup>9-11</sup>; however, the influence of their structure is still under research<sup>12,13</sup>. Several authors have studied the synthesis of branched PAMs<sup>14</sup> and the possibility to improve sheet formation with high retention of fines and fillers. They observed that flocculation induced by branched PAMs was slower than the one induced by a linear PAM with similar molecular weight and charge density, and that the formed flocs were smaller and stronger<sup>15,16</sup>. Furthermore, some authors have observed that, in presence of high hydrodynamic forces, flocculation efficiency of branched PAMs was higher than the one of the linear ones. Therefore, the use of branched PAM could improve retention and drainage in paper mills<sup>12,13</sup>. The difficulty of producing PAMs with highly controlled branching has caused studies of the branching effect to be limited to the comparison of linear PAMs with uncontrolled branched PAMs and star polymers (polymers with a very high

branching, which gives them a star structure). Now, it is possible to produce highly controlled branched PAMs with very high molecular weight at industrial scale<sup>14</sup>. Therefore, the next step is to compare the effect of branching grade on flocculation processes, which has been the main aim of this research.

## 2. Materials and methods

ECF eucalyptus kraft pulp has been used with a consistency of 1% containing 20% of ground calcium carbonate (GCC) on dry fibres. This suspension contains the most common hardwood fibres and mineral filler used in European papermaking industry<sup>17</sup>.

Cationic polyacrylamides (CPAMs) of very high molecular weight, around  $12 \cdot 10^6$  g/mol, different charge densities and different homogeneous branching grades, whose properties are summarised in the table 1, have been used as flocculants. Information on the structure and characteristics of these branched CPAMs has been published before<sup>14</sup>.

**Table 1.** Studied PAMs.

Branches per molecule	Charge density (%)
0	20 / 90
1	20
2	20
3	20
4	90
16	90

### ***Preparation of suspensions and additives***

To prepare the pulp suspensions, 50 g of cellulose fibres were soaked in 2 L of water during at least 12 hours, in order to swell them. After that, they were disintegrated at 6000 revolutions in a normalized disintegrator (T-215) and suspension was diluted by adding 4 L of water. Then, 10 g of GCC were added and the mixture was stirring in a homogeniser at 425 rpm during 30 minutes.

The CPAMs were supplied in emulsion. They were diluted to 0.2%w in ultrapure water. To avoid the effect of ageing, flocculants were prepared the same day when they were used and they were matured during 90 minutes, before using them<sup>18,19</sup>.

### ***Experimental procedure***

The evolution of the flocculation, deflocculation and reflocculation processes was monitored in real time by using a M500L FBRM probe supplied by Mettler Toledo (USA). This device allows us to obtain the chord size distribution of particles and aggregates in the suspension<sup>20,21</sup>.

The FBRM device provides a laser light shaft of 791 nm of wave length, which is focused by a lens, which rotates at 2268 rpm, in a focal point at 20  $\mu\text{m}$  of the outer surface of the sapphire window, which is at the end of the probe introduced in the sample. The rotation of the lens produces a uniform circular translation of the focal point in the parallel plane to the window's surface. When a particle intercepts the trajectory of the focal point, the reflected light is conducted to the detector, which receives pulses of light that translates into amplified electrical pulses and it is transformed into digital information that can be stored and processed. The duration of each light pulse is directly proportional to the chord sizes of the particle that has intercepted the focal point path. Chord sizes

between 1 and 1000  $\mu\text{m}$  are collecting during a regular measurement time after which a histogram of the collected chord sizes is displayed. This distribution is characteristic of the form, size and concentration of the particles in suspension<sup>22,23</sup>. A measurement time of 5 s was selected to monitor flocculation, deflocculation and reflocculation processes, getting distributions which are representative of particles population with high answer speed and with a minimum ground signal<sup>20,21</sup>.

In a typical flocculation trial, the FBRM probe was placed in the suspension stirred at 400 rpm. After 1 minute stirring, the flocculant was added. This caused the flocculation of the particles in suspension. Stirring was kept constant during 6 minutes. Then, the stirring speed was increase to 800 rpm during 1 minute to break down the flocs. Finally, it was decreased again to 400 rpm to study the reflocculation process.

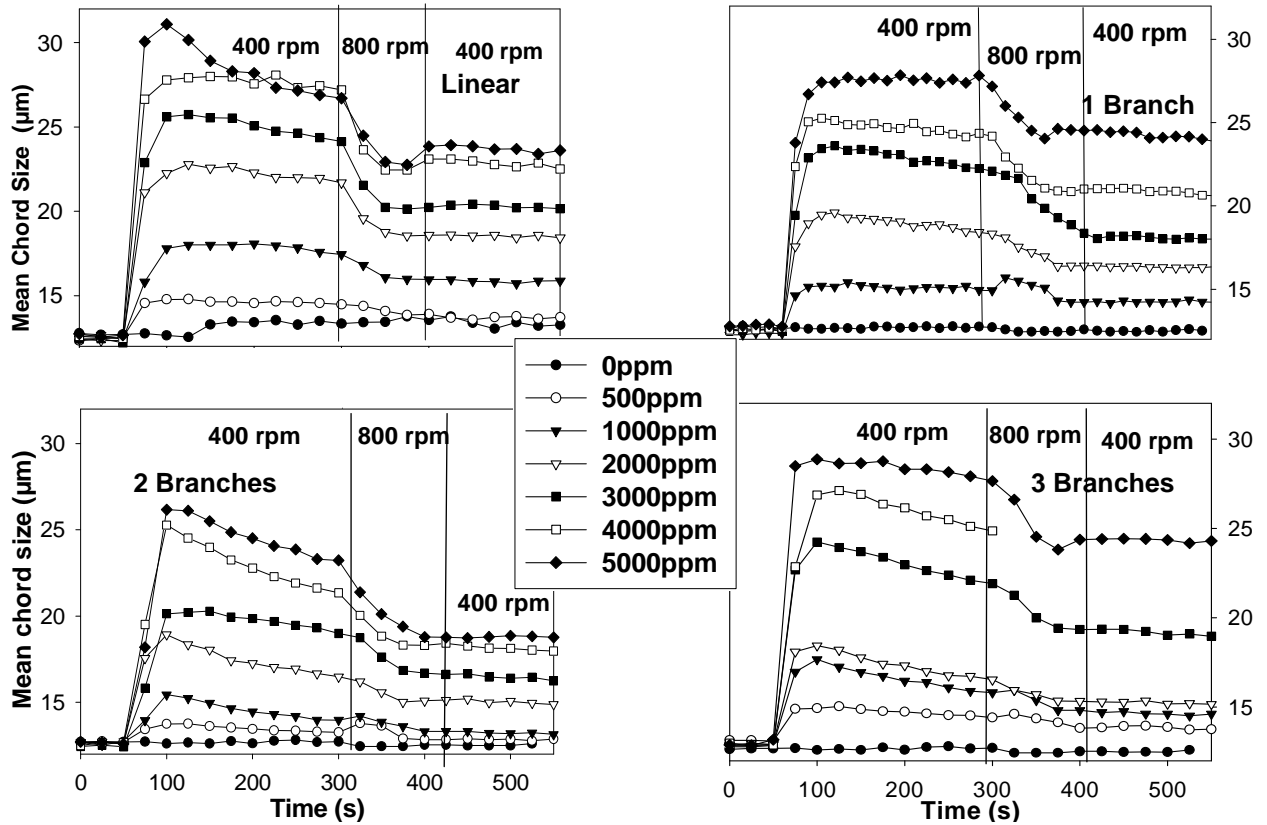
### **3. Results and discussion**

#### ***Effect of the structure of CPAM with low charge density***

The evolution of the mean chord size during flocculation, deflocculation and reflocculation in presence of CPAM with a charge density of 20% and four different branching grades is presented in figure 1.

The addition of flocculant induced the formation of flocs that were stable at 400 rpm, as shown by the fast increase of the mean chord size just after adding the flocculant and by the stability of its value before the stirring increase. When stirring increased, 4 minutes after the addition of the flocculant, the largest flocs were broken, but some of the flocs were strong enough to keep high the value of the mean chord size during deflocculation stage. However, these flocs had very low

reflocculation ability, as shown by the null mean chord size increase after the stirring reduction; small reflocculation was only observed at high doses of flocculant.



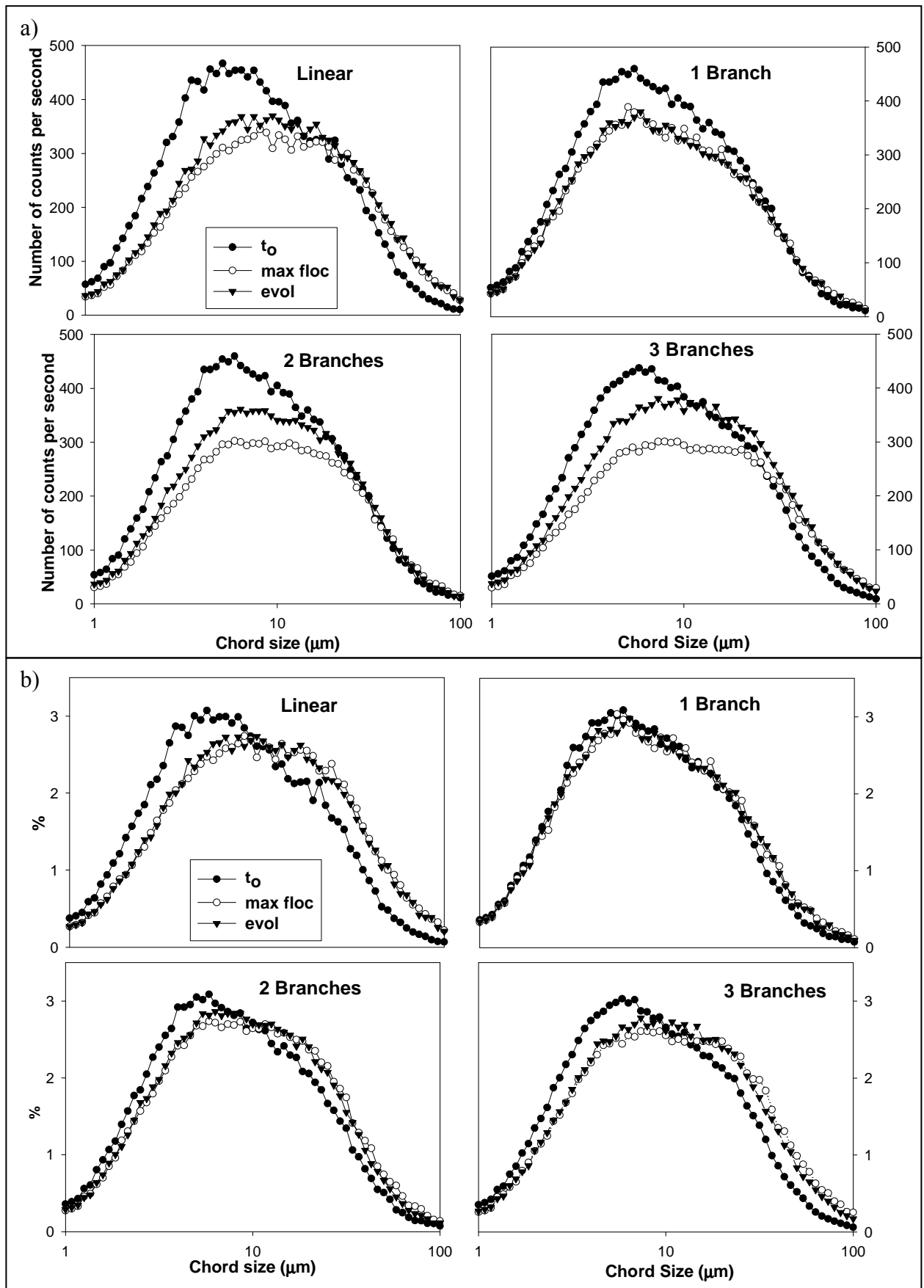
**Figure 1.** Effect of branching grade on the mean chord size evolutions when different doses of CPAM with a charge density of 20% were added.

The CPAM branching grade affected the mean chord size achieved after flocculation. This effect depended on CPAM doses. In general, the presence of branches reduces the maximum mean chord size obtained after flocculation comparing with the values obtained with the linear CPAM.

Flocs induced with 5000 ppm of linear flocculant were the most unstable ones at 400 rpm. This is due not only to the high size of flocs, being the largest flocs broken easily. It is also possible that the excess of polymer, which increased the repulsion between chains adsorbed on different particles<sup>2</sup>, contributing to increase instability. This effect was not observed when the branching grade increased to 3 branches. This is because the hydrodynamic volume of branched polymers decreases

when branching grade increases, thus at the same flocculant doses, the repulsion between chains decreases because the number of molecules necessary to cover the surfaces increases. This fact made easier the formation of bonds between particles in pulp suspension and increased their strength.

Figure 2 shows the chord size distributions obtained at different moments: before the addition of flocculant ( $t_0$ ), when the maximum mean chord size was achieved (max flocc) and after the evolution of the induced flocs (evol), i.e. just before increasing the stirring to induce deflocculation process. Chord size distributions are function of size and shape of particles in the suspension. Asymmetric shape is a result of the higher number of small chord sizes due to the higher number of filler and fine particles with respect to fibres, although their lower mass. When the maximum mean chord size was achieved, the area under distribution curves was lower than the one obtained before flocculation, and distributions moved towards higher chord sizes. Figure 2b shows this displacement clearer. It indicates the decrease of particle number concentration and the increase in particle size. This effect was more remarkable when the used CPAM was linear or had three branches per molecule. The area of the distributions with the maximum mean chord size is smaller than the ones obtained after the evolution of the flocs, however the normalised distributions are not displaced. This indicates that more particles were counted, but with similar size distribution. This confirms that the flocculation of particles smaller than  $1 \mu\text{m}$  to form flocs is the predominant effect during the evolution stage.



**Figure 2.** Effect of branching grade on chord size distributions during the flocculation process and after floc evolution induced by 1000 ppm of CPAM with charge density of 20%. a) distributions, b) normalised distributions.



When the charge density of very high molecular weight polymers is low, chains configuration in the solution is not extended, and only the external part of the polymer ball and the tails or coils can interact with particles. Increasing branching has two opposite effects:

1. Reduces the hydrodynamic volume, decreasing the distance among particles in a floc and, therefore, the frequency of efficient collisions.
2. Increases the stiffness of the polymer and the number of tails and coils that can interact with particles to form bridges among them, that increases collision efficiency.

Therefore, the global effect is the balance between these two ones. Adding one branch per molecule to the low charged CPAM reduced the floc size obtained with 1000 ppm as shown in figures 1 and 2, because of the hydrodynamic volume reduction. Furthermore, it reduced the flocculation of small particles as it can be observed comparing the left part of the distributions (from 1  $\mu\text{m}$  to 10  $\mu\text{m}$ ) obtained with the linear CPAM and the one with one branch per molecule. The decrease in the number of counts with chord sizes smaller than 10  $\mu\text{m}$  is higher when linear CPAM was used (figure 2). Distributions show that the number of counts at the 1  $\mu\text{m}$  limit decreased when CPAM was added, indicating that particles with chord sizes of 1  $\mu\text{m}$  and smaller were attached to other particles to form larger flocs. When 1000 ppm of CPAM were used, this decrease was higher in the case of linear CPAM than in the case of CPAM with 1 branch per molecule. Mean chord size decreased also when CPAM had two branches per molecule; however flocculation of small particles increased due to the higher number of tails and the higher stiffness of the chain. When CPAM had three branches per molecule the increase in the number of tails free to interact with particles was high enough to further flocculate the system, increasing the maximum floc size and the floc size after the evolution of the system.

Chord size distribution after the evolution of flocs obtained in presence of the CPAM with 2 or 3 branches per molecule had a higher area than the one obtained with the highest mean chord size.

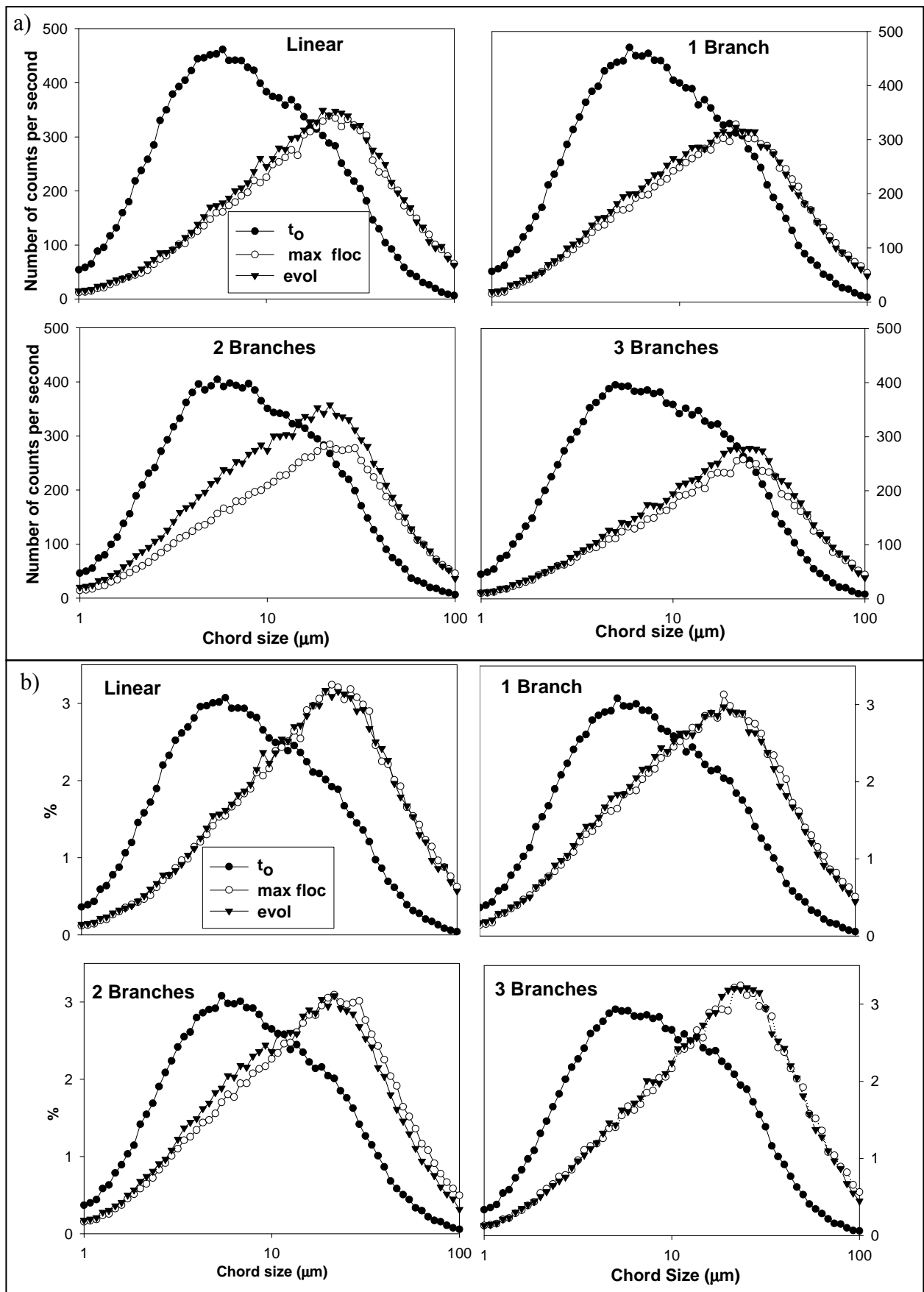
Moreover, there is not a reduction of the number of counts with large chord size, but there is an increase in the number of counts of lower sizes. Therefore, although some of the largest flocs could be destroyed during the evolution of the system, the main process during this stage was the flocculation of the small particles, some of them smaller than 1  $\mu\text{m}$ . These particles cannot be measured because of their small size (the detection limit of the technique is 1  $\mu\text{m}$ ). However, when they aggregate, they form flocs that can overcome this limit and be measured. These small flocs reduce the mean chord size. This process is slower than the flocculation of the large particles and, therefore, it reduces the mean chord size of the distribution after reaching a maximum value.

Figure 3 shows the distributions of mean chord sizes obtained with 4000 ppm of flocculant. When doses increased, distributions after flocculation moved towards larger chord sizes, indicating the increase in the size of the induced flocs. On the other side, after reaching the maximum mean chord size, the changes in the distributions obtained during the evolution of the flocs were small and normalised distributions were shifted only very slightly towards lower chord sizes, except when CPAM had two branches per molecule, which shows higher changes. This indicates that:

- Most of formed flocs were very stable at 400 rpm. Only the largest ones were broken.
- Flocculation of small particles to form small flocs was not predominant after reaching the maximum mean chord size.

Both phenomena contributes to decrease the mean chord size during evolution stage (figure 1).

In case of using CPAM with 2 branches, the number of counts with chord sizes smaller than 60  $\mu\text{m}$  increased during evolution stage while the number of larger counts only decreased slightly (Figure 3a). The increase in the number of counts smaller than 60  $\mu\text{m}$  is due not only to the breakage of some of the largest flocs, but also to the flocculation of particles smaller than 1  $\mu\text{m}$  to form small flocs.



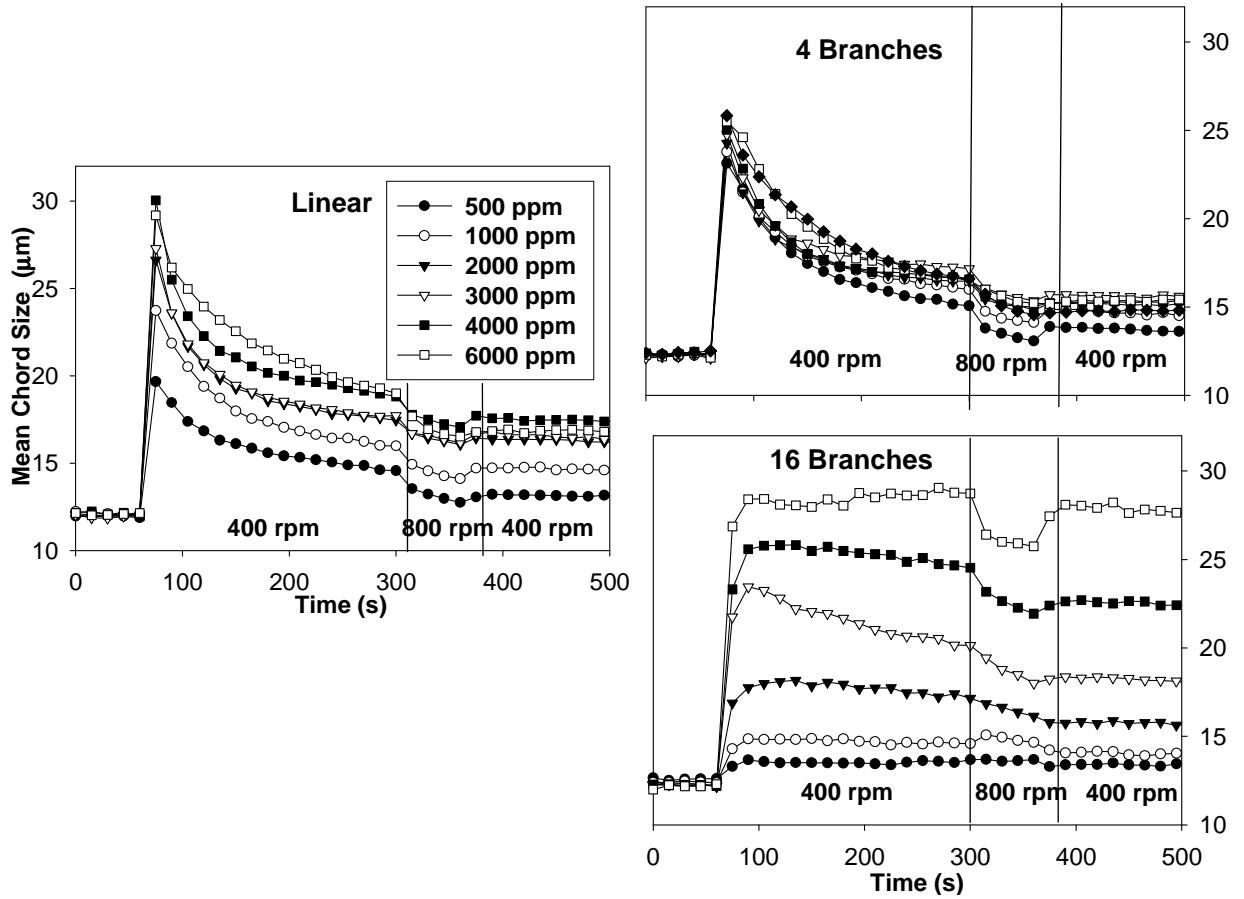
**Figure 3.** Effect of branching grade on chord size distributions during the flocculation process and after floc evolution induced by 4000 ppm of CPAM with charge density of 20%. a) distributions, b) normalised distributions.

When flocculant dose increased, there were more molecules of the polymer in suspension, so more bonds between particles can be formed. In addition, in presence of 4000 ppm of CPAM the coverage of particles surfaces was higher than it was when CPAM dose was 1000 ppm and there were less available gaps in the surface to flatten the chains of polymer. Thus, stability of the formed bonds increased and the effect of polymer structure on its flattening decreased. After the polymer adsorption was finished and maximum floc size was achieved, flocculation of small particles did not form small flocs that decrease the mean chord size, but they were attached to large flocs during flocculation as shown by the decrease in the number of counts with chord sizes in the limit of 1  $\mu\text{m}$  and by the reduction of the shape in the left part of the distribution when CPAM was added to the suspension.

#### ***Effect of the structure of CPAM with high charge density***

Figure 4 shows that when the charge density of CPAM is high, the effect of CPAM structure on their behaviour was very high. Flocs induced by CPAM with 90% charge density were unstable, except for the CPAM with 16 branches per molecule due to the high stiffness of its configuration. In this case, linear CPAM has an extended and stiffness configuration in solution because of the electrostatic repulsion among charged groups<sup>7</sup>. However, when it adsorbed on a charged particle, its conformation evolved towards a flat configuration due to the high interaction between particle surface and polymer chain<sup>26</sup>. This causes a low stability of the flocculated system. For low doses, flocculation is poor. When the flocculant dose increases, the particle surface free to interact with the polymer is reduced and the percentage of polymer chains adsorbed with an extended conformation is increased. However, with the time, the configuration of the polymer chains evolved towards a flat conformation, covering the particle surfaces, and part of the initially formed bridges were broken.

However, the reduction of the mean chord size could be also due to the flocculation of particles smaller than 1  $\mu\text{m}$  that cannot be measured before their flocculation, but that form small flocs that reduce the mean chord size.



**Figure 4.** Effect of branching grade on mean chord evolutions induced by CPAM with charge density of 90%.

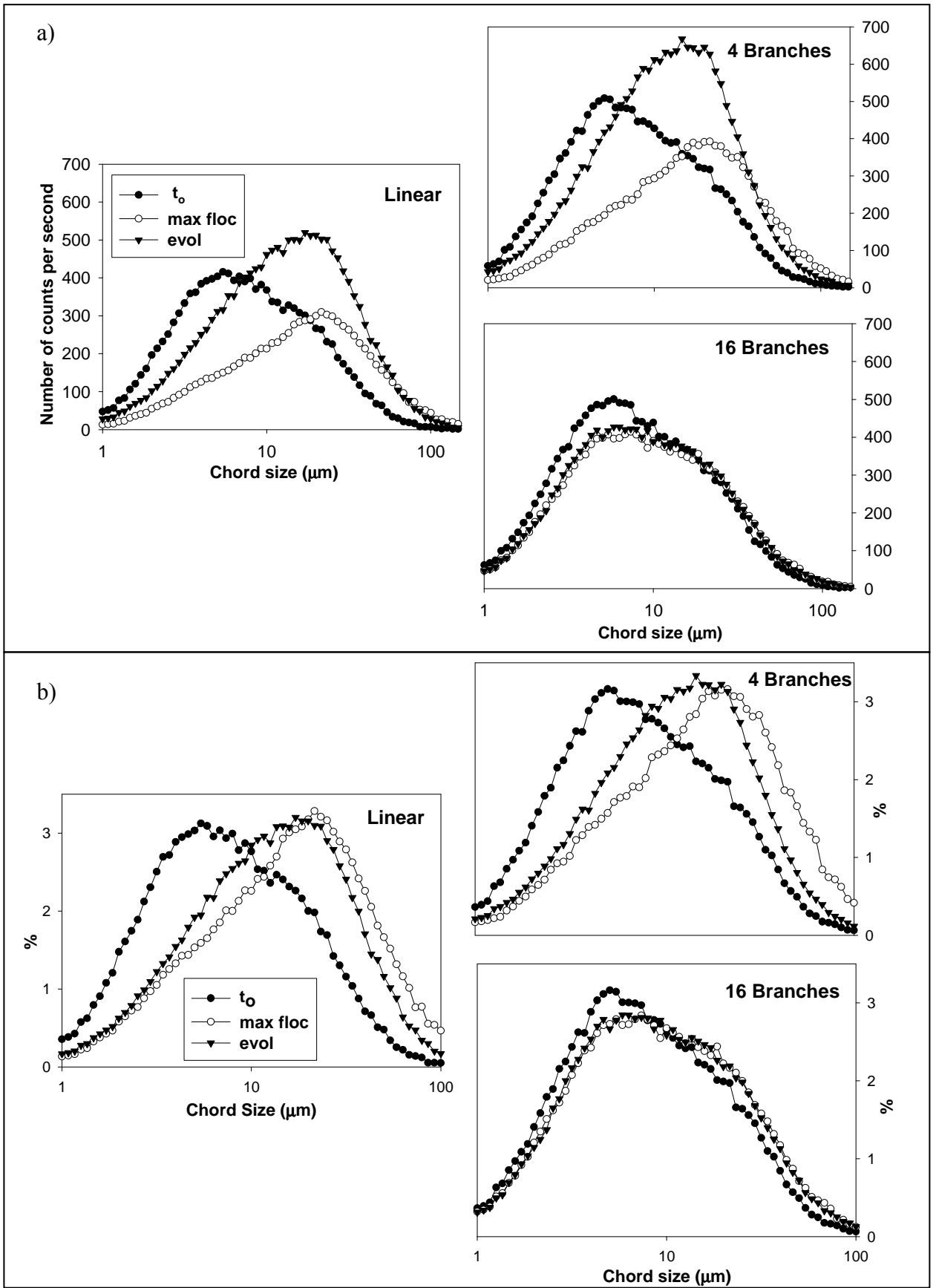
To know the reason of the mean chord size evolution, it is necessary to compare the chord size distributions (figure 5). The area under the curve obtained after the evolution of the system was higher and contained larger chord sizes than the initial one (figure 5a). Therefore, more and larger particles were measured after floc evolution. However, the area of the distribution obtained when maximum mean chord size was achieved was the lowest and it contained the largest values of chord size. These two characteristics confirm that particles smaller than 1  $\mu\text{m}$  (which were not detected by FBRM at the beginning) are flocculated during the evolution stage, and the displacement of the normalised distribution towards lower chord sizes during the evolution stage confirms that the

largest flocs induced by linear and low branching grade polymers could break down to form new small particles. Branches increase polymer stiffness, which makes more difficult its adsorption with flat conformation. However, the main effect of polymer structure was the reduction of the hydrodynamic volume of the chains, because the stiffness was already high without branches due to the high charge density that causes strong repulsive electrostatic forces among charged groups of the chains. Consequently, strong differences in the evolution of the formed flocs were observed when CPAM branching increased to 16.

With 500 ppm, the highest mean chord size was achieved with the CPAM of four branches, but for higher doses the maximum mean chord size obtained with his CPAM was lower than the one obtained with the two other flocculants. This CPAM has an hydrodynamic volume between the other two, but its structure is stiff and repulsion among chain segments allowed the presence of loops and tails of the adsorbed chains and its interaction with particles when flocculant dose was low, despite of its high charge density and the presence of enough free surface on particles. Therefore, flocculation achieved with low doses of this CPAM was higher than the one achieved with the linear flocculant. The small hydrodynamic volume of this branched CPAM reduced the floc size obtained with high doses. The effect of flocculant dose on flocculation and on floc properties was very low, in this case. This could indicate that regardless the doses added, the same amount of polymer was adsorbed onto particles. Low amount of adsorbed chains could be enough to form bridges among particles. Because of the low hydrodynamic volume, the formation of flocs required a closer approach of the particles. This could limit the adsorption of more chains near the space between the joined particles to form more bridges<sup>26</sup>. This could reduce floc strength, as it can be observed in figure 5, which shows that breakage of large flocs was higher for the CPAM with four branches per molecule. The flocculant with sixteen branches per molecule induced the formation of very stable flocs and with high reflocculation ability. This flocculant has a very low hydrodynamic volume

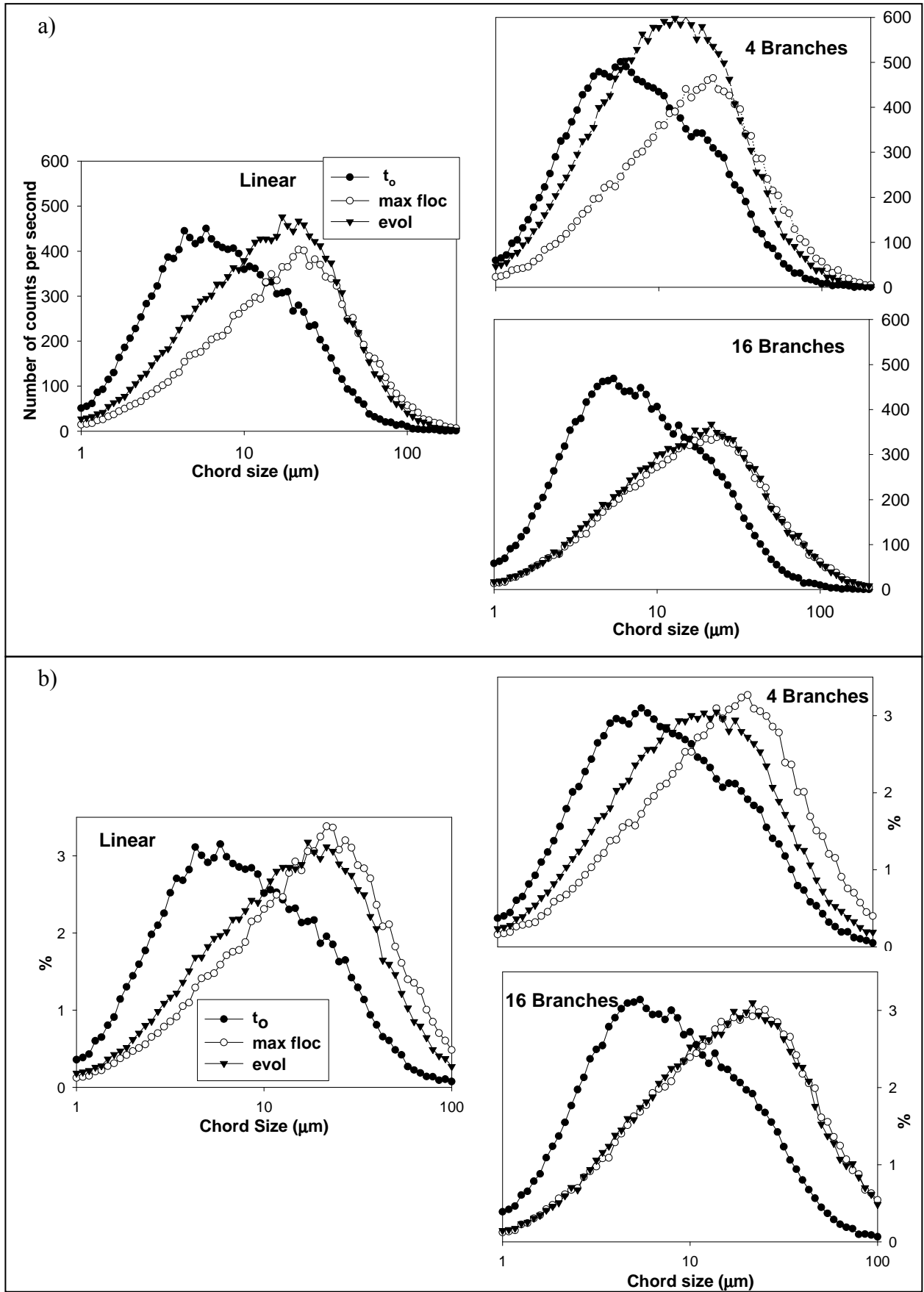
despite of its very high molecular weight<sup>27</sup>. Consequently, its structure is very stiff and stable, but the formation of bridges between particles is more difficult due to its low hydrodynamic volume. Therefore, the predominant flocculation mechanism could be patching. Maximum patching flocculation is obtained when coverage of particles is around 50%<sup>28</sup>. The low hydrodynamic volume of this CPAM increased the dose required to reach this coverage grade. Therefore, this flocculation mechanism explains why the flocs obtained with doses lower than 4000 ppm were smaller than the ones obtained with the same doses of linear or low branching grade CPAMs. Electrostatic reversible forces were responsible of flocculation induced by highly charged branched CPAM. Consequently, formed flocs were very stable and reflocculation ability was high, as shown by the evolution of the mean chord size after decreasing the stirring speed, that reach a value very similar to the one measured before deflocculation stage (figure 4).

Figure 6 shows that when linear CPAM dose increased, flocculation of particles in the suspension and flocs size increased due to the increase of the coverage, which reduced the flattening of linear CPAM due to steric repulsion among adsorbed chains. For the CPAM with 16 branches, higher doses increased the floc size due to the increase of the number of patches. During the evolution stage, the breakage of large flocs ( $>50 \mu\text{m}$ ) was more important than the flocculation of particles smaller than  $1 \mu\text{m}$ , except in the case of CPAM with 16 branches as shown by the decrease in the number of counts with large chord sizes (figure 6a) and the displacement of the normalised distribution towards lower chord sizes (figure 6b) when linear or 4 branches CPAM were used. It indicates that most of the aggregation of these small particles was fast enough to take place during the flocculation stage. For CPAM with 16 branches, the difference between the distribution with the maximum mean chord size and the one obtained after the evolution of flocs is very low indicating the high stability of the flocs at 400 rpm.



**Figure 5.** Effect of branching grade on chord size distributions during the flocculation process induced by 1000 ppm. CPAM with charge density of 90%. a) distributions, b) normalised distributions.





**Figure 6.** Effect of branching grade on chord size distributions during the flocculation process induced by 4000 ppm. CPAM with charge density of 90%. a) distributions, b) normalised distributions.

To have more complete information of the effect of flocculant dose on the system, the chord size distributions obtained with different doses of each flocculant were compared at two different moments: when maximum mean chord size was achieved and just after the evolution stage (figures 7 and 8).

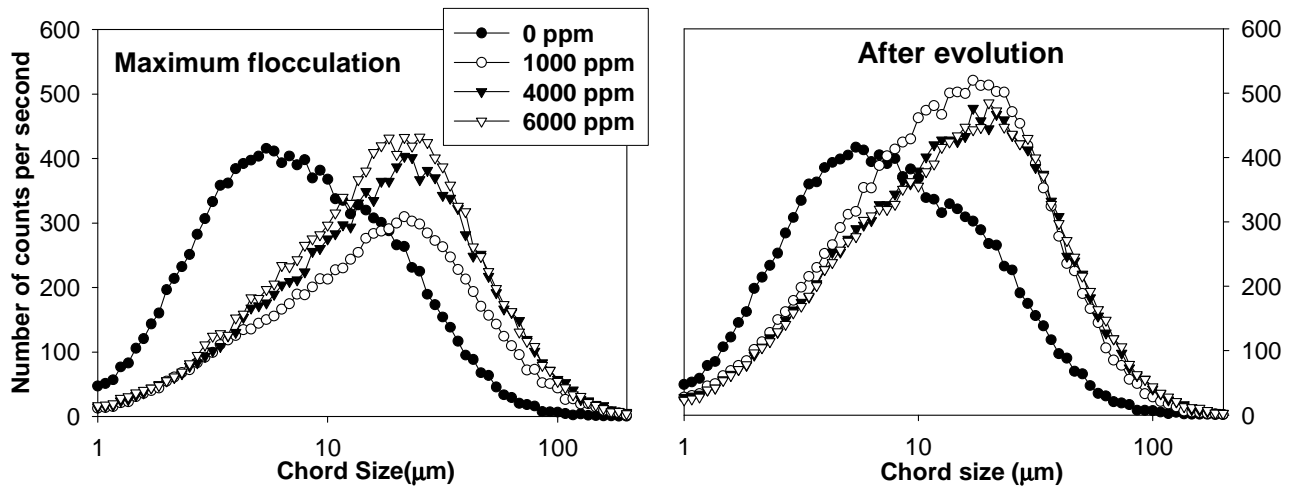
Flocculation induced by 4000 ppm and 6000 ppm of linear CPAM provided very similar normalised distributions at the maximum mean chord size (figure 8a) and the area under the not normalised curves was higher than the one obtained with 1000 ppm and a higher number of counts was obtained for all the chord lengths. It indicates that particles smaller than 1  $\mu\text{m}$  flocculate, increasing the measured number of particles for all sizes, this effect increases with the dose. After the evolution stage, distribution for 1000 ppm was slightly displaced towards lower chord lengths with respect to the ones obtained in presence of higher flocculant doses (figures 7a and 8a).

The mean chord size decreased during the evolution of the system (figure 4) because of two phenomena:

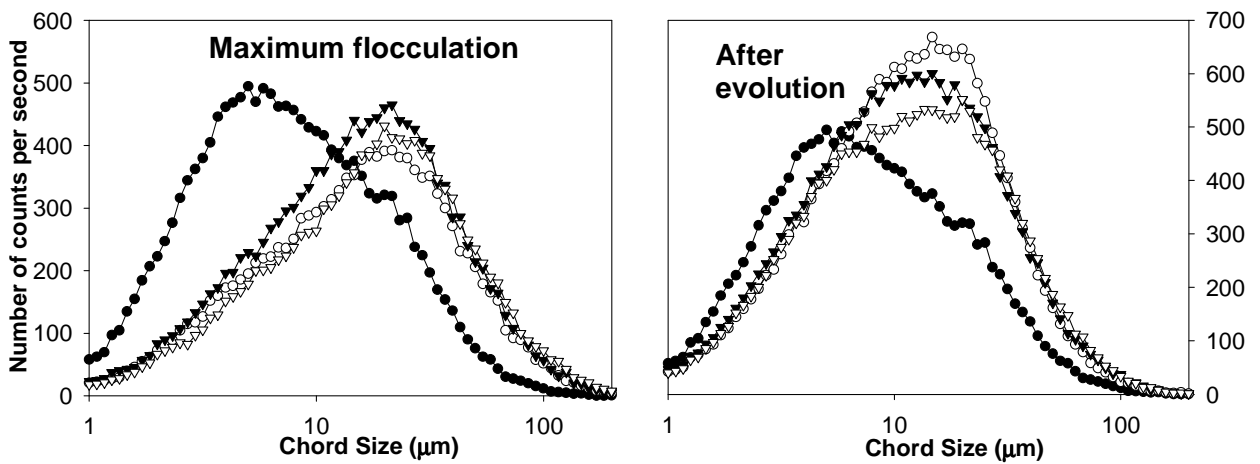
1. Flocculation of particles smaller than 1  $\mu\text{m}$ , which was the predominant effect (figure 6).
2. Dispersion of large flocs, that was low as shown in figure 6b.

On the other hand, comparing the distributions shown in figure 7a, it can be observed that the area under the chord sizes distributions during evolution stage increased with respect to the maximum mean chord size, when dose was 1000 ppm and 4000 ppm, and that differences between the distributions with the maximum mean chord size and the ones obtained just after the evolution stage decreased with linear CPAM doses and thus, distributions obtained after the evolution stage with the three doses were very similar. Therefore, dispersion of large flocs and flocculation of small

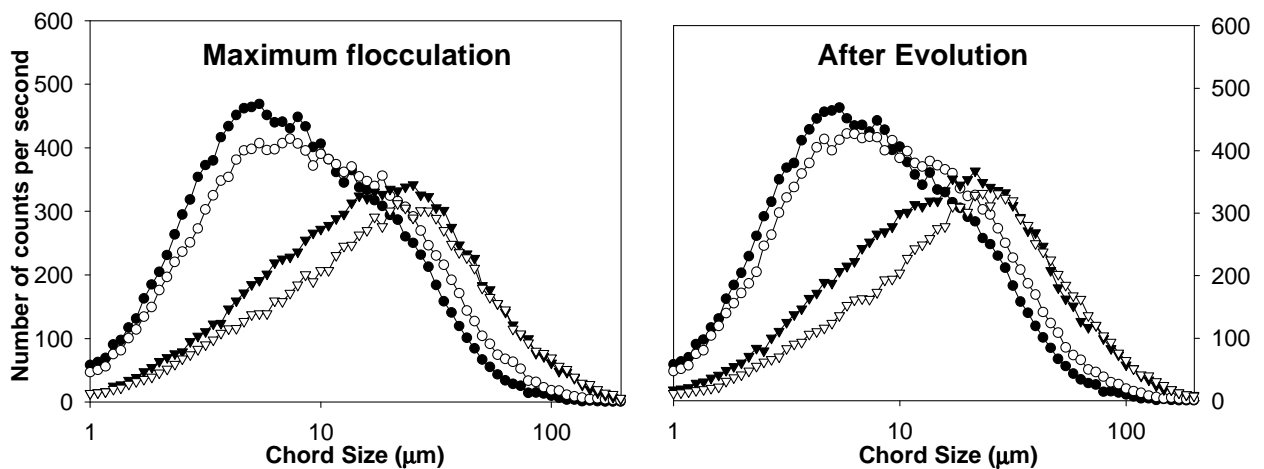
particles took place in the three cases during the evolution stage, but its extension decreased with the linear CPAM doses.



a) Linear.

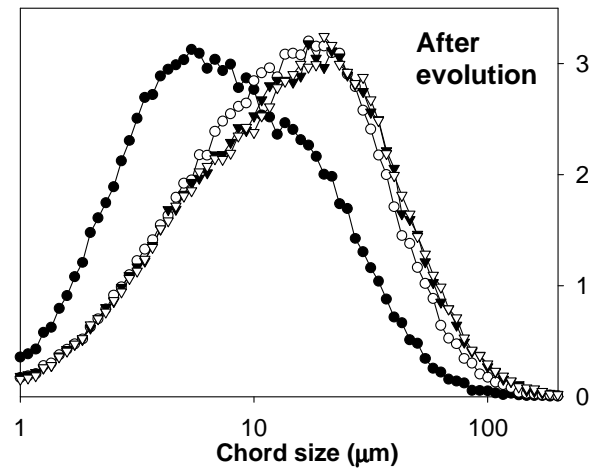
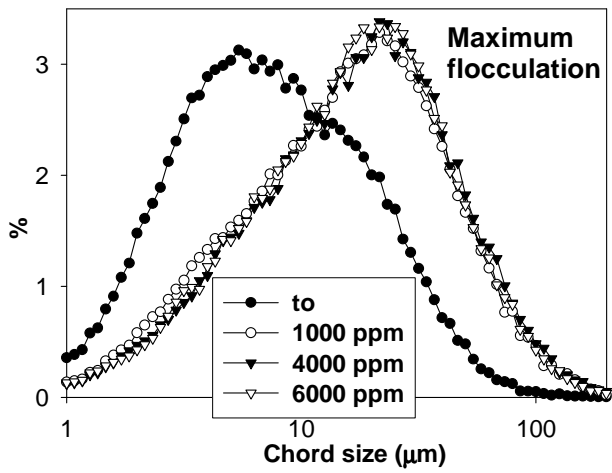


b) Four branches per molecule.

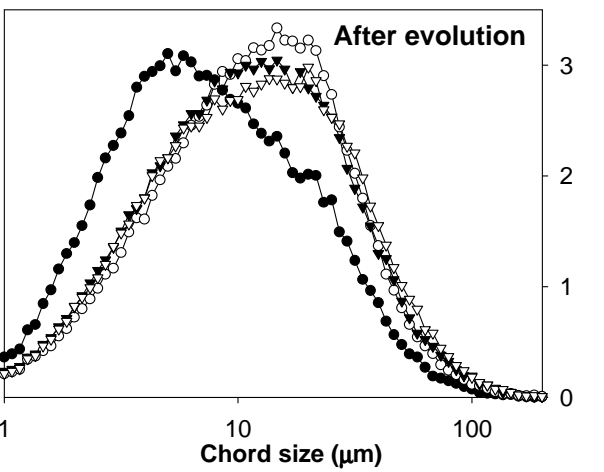
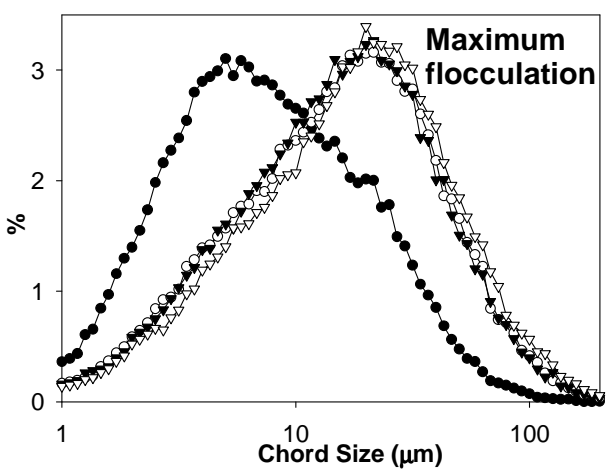


c) Sixteen branches per molecule.

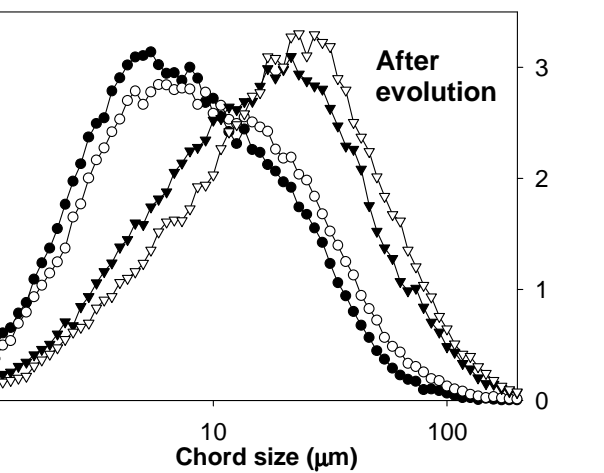
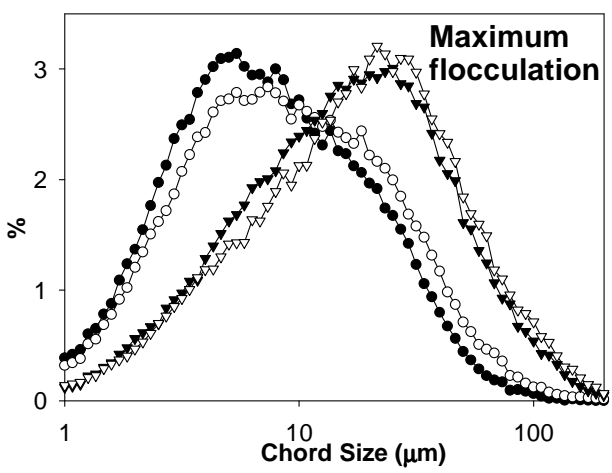
Figure 7. Chord size distributions CPAM with charge density of 90%.



a) Linear.



b) Four branches per molecule.



c) Sixteen branches per molecule.

Figure 8. Normalised chord size distributions CPAM with charge density of 90%.

Figures 7b and 8b corroborate the low effect of the doses of CPAM with four branches per molecule on flocculation, and show that its main effect was observed after the evolution of the system.

CPAM with 16 branches per molecule induced the formation of flocs much more stable than the ones induced by the other two CPAMs (figures 5b and 6b). Furthermore, flocculation of particles smaller than 1  $\mu\text{m}$  did not take place during evolution stage regardless the used dose, as shown in figure 6c, where there are no remarkable differences between the distributions with maximum mean chord size and the ones obtained after the evolution of flocs. Furthermore, the areas under these distributions are lower than the area under the initial one (without flocculant). This indicates that the flocculation of particles smaller than 1  $\mu\text{m}$  to form small flocs is less favoured by this highly branched CPAM, or that they aggregate to fibers or to large flocs.

The effect of polymer dose on flocculation was higher than in the other two cases. A few small flocs were only formed when a dose of 1000 ppm of this CPAM was used, as shows the low displacement of the distribution towards longer chord lengths (figures 7c and 8c). This is because of the low hydrodynamic volume of this polymer, which could cause that part of the chains were not able to exceed the double electrostatic layer to interact with other particles. Furthermore, the coverage required for efficient patching flocculation is higher than the one required for bridging.

#### **4. Conclusions**

The effect of CPAMs structure on flocculation process and induced flocs properties depends on charge density. At the experimental conditions, when CPAM had a low charge density, branching effect on stiffness and hydrodynamic volume of the polymer chains affected considerably the

flocculation process and the floc properties. However, when CPAM had a very high charge density, the highest effect was the reduction of the hydrodynamic volume at high branching grades, because it changed the flocculation mechanism from bridging to patching. However, the increase of stiffness improved flocculation induced by low dose of CPAM with four branches per chain, in the case of high charge density.

CPAMs with a charge density of 20% induced the formation of hard flocs with low reflocculation ability. Floc size decreased slightly and the flocculation of particles lower than 1  $\mu\text{m}$  increased to form small flocs during the evolution stage with the branching grade, when CPAM dose was low.

When CPAM had high charge density, moderate branching grade increased flocculation induced by low doses of CPAM and reduced the effect of CPAM dose on flocculation and floc properties in the doses interval tried. However, when branching grade of this CPAM was very high (16 branches), the predominant flocculation mechanism was patching, so the formed flocs were more stable and the system had a high reflocculation ability.

### **Acknowledgments**

The authors wish to thank AQUA+TECH for the supply of polyacrylamides, the Community of Madrid for supporting the project “Producción limpia de papel reciclado: Hacia la sostenibilidad en la producción de papel en la Comunidad de Madrid” PROLIPAPEL (S-0505/AMB/0100) and the European Union for supporting the project “Novel Device to Study Pulp Suspensions Behaviour in order to Move towards Zero Energy Losses in Papermaking”, NODESZELOSS (COOP-CT-2004/513117).

## References

- (1) Fuente, E.; Blanco, A.; Negro, C.; Pelach, M.A.; Mutje, P.; Tijero, J. Study of filler flocculation mechanisms and floc properties induced by polyethylenimine. *Ind. Eng. Chem. Res.* **2005**, 44(15), 5616-5621.
- (2) Blanco, A.; Negro, C.; Fuente, E.; Tijero J. Effect of Shearing Forces and Flocculant Overdose on Filler Flocculation Mechanisms and Floc Properties. *Ind. Eng. Chem. Res.* **2005**, 44, 9105-9112.
- (3) Negro, C.; Fuente, E.; Blanco, A.; Tijero, J. Flocculation mechanism induced by phenolic resin/PEO and floc properties. *AIChE J.* **2005**, 51(3), 1022-1031.
- (4) Yan, H.; Lindstrom, T.; Christiermin, M. Some ways to decrease fibre suspension flocculation and improve sheet formation. *Nordic Pulp Pap. Res. J.* **2006**, 21(1), 36-42.
- (5) Cadotte, M.; Tellier, M.E.; Blanco, A.; Fuente, E.; van de Ven T.G.M.; Paris, J. Flocculation, retention and drainage in papermaking: A comparative study of some polymeric additives. *Can. J. Chem. Eng.* **2007**, 85(2), 240-248.
- (6) Buchholz, F.L. Polyacrylamides and Poly (Acrylic Acids) in Ullmann's. Encyclopaedia of Industrial Chemistry; VCH Publishers, Inc. 1992, 21, 143-156.
- (7) Ma, M.; Zhu, S. Grafting polyelectrolytes onto polyacrylamide for flocculation. Polymer synthesis and characterization. *Colloid Polym. Sci.* **1999**, 277(2-3), 115-122.
- (8) Odberg, L.; Wagberg, L. Polymer conformation and flocculation. *Papier*, **1989**, 43(10A), V37-V38.

- (9) Vanerek, A.; Alince, B.; Van de Ven, T.G.M. Interaction of Calcium Carbonate Fillers with Pulp Fibres: Effect of Surface Charge and Cationic Polyelectrolytes. *J. Pulp Pap. Sci.* **2000**, 26(9), 317-322.
- (10) Ariffin, A.; Shatat, R.S.A.; Norulaini, A.R.N.; Omar, A.K.M. Synthetic polyelectrolytes of varying charge densities but similar molar mass based on acrylamide and their applications on palm oil mill effluent treatment. *Desalination.* **2005**, 173, 201-208.
- (11) Nasser, M. S.; James, A. E. Effect of polyacrylamide polymers on floc size and rheological behaviour of kaolinite suspensions. *Colloid Surf. A-Physicochem. Eng. Asp.* **2007**, 301, 311-322.
- (12) Brouillette, F.; Morneau, D.; Chabot, B.; Daneault, C. Paper formation improvement through the use of new structured polymers and microparticle technology. *Pulp Pap. Canada.* **2004**, 105(5), 31-35.
- (13) Brouillette, F.; Morneau, D.; Chabot, B.; Daneault, C. A new microparticulate system to improve retention/ drainage in fine paper manufacturing. *Appita J.* **2005**, 58(1), 47-51.
- (14) Hernandez, J.; Hunkeler, D. Polyacrylamide Copolymeric Flocculants with Homogeneous Branching: Heterophase Synthesis and Characterization. *Polym. News.* **2004**, 29, 239-246.
- (15) Shin, J.H.; Han, S. H.; Sohn, C.; Ow, S.K.; Mah, S. Highly branched cationic polyelectrolytes: Fines retention. *Tappi J.* **1997**, 80(10), 185-189.
- (16) Shin, J.H.; Han, S. H.; Sohn, C.; Ow, S.K.; Mah, S. Highly branched cationic polyelectrolytes: Filler flocculation. *Tappi J.* **1997**, 80(11), 179-185.
- (17) Strutz, M.; Blitx, T. Calcium carbonate pigments custom fit for the groundwood market. PAPTAC 89<sup>th</sup> Ann. Meeting. 2003. Montreal, QC, Canada, 27-30.



- (18) Sastry, N. V.; Dave, P.N. Valand, M.K. Dilute solution behaviour of polyacrylamides in aqueous media. *Eur. Polym. J.* **1999**, 35(3), 517-525.
- (19) Owen, A.T.; Fawell, P.D.; Swift, J.D.; Farrow, J.B. The impact of polyacrylamide flocculant solution age on flocculation performance. *Int. J. Miner. Process.* **2002**, 67, 123-144.
- (20) Blanco, A.; Fuente, E.; Monte, M.C.; Negro, C.; Tijero J. Focused Beam Reflectant Measurement as a tool to measure flocculation. *Tappi J.* **2002**, 1(10), 14-20.
- (21) Blanco, A.; Fuente, E.; Negro, C.; Tijero J. Flocculation monitoring: Focused Beam Reflectance Measurements as a measurement tool. *Can. J. Chem. Eng.* **2002**, 80(4), 734-740.
- (22) Li, M.; Wilkinson, D. Determination of non-spherical particle size distribution from chord length measurements. Part I: theoretical analysis. *Chem Eng Sci.* **2005**, 60, 3251-3265.
- (23) Li, M.; Wilkinson, D. Patchigolla, K. Determination of non-spherical particle size distribution from chord length measurements. Part II: Experimental validation. *Chem Eng Sci.* **2005**, 60, 4992-5003.
- (24) Yoon, S.Y.; Deng, Y. Flocculation and reflocculation of clay suspension by different polymer systems under turbulent conditions. *J. Colloid. Interf. Sci.* **2004**. 278, 139-145.
- (25) Yu, X.; Somasundaran, P. Kinetics of polymer conformational changes and its role in flocculation. 1996. *J. Colloid. Interf. Sci.* **1996**. 178, 770- 774.
- (26) Solberg, D.; Wagberg, L. On the mechanism of cationic-polyacrylamide- induced flocculation and re-dispersion of a pulp fiber dispersion. *Nordic Pulp Pap. Res. J.* **2003**, 18(1), 51-55.

(27) Biswal, D.R.; Singh, R.P. Characterisation of carboxymethyl cellulose and polyacrylamide graft copolymer. *Carbohydr. Polym.* **2004**, 57(4), 379-387.

(28) Leong, Y.K. Interparticle forces arising from an adsorbed strong polyelectrolyte in colloidal dispersions: charged patch attraction. *Colloid Polym. Sci.* **1999**, 277(4), 299-305.