

## Flocculation Efficiency of Chitosan for Papermaking Applications

Raluca Nicu,<sup>a</sup> Elena Bobu,<sup>a,\*</sup> Ruben Miranda,<sup>b</sup> and Angeles Blanco<sup>b</sup>

There is a large interest in bio-polymers as environment-friendly alternatives to synthetic additives in papermaking. In this work, the behavior of three chitosans with different molecular weights and cationic charges were investigated as flocculation additives in papermaking on two systems: calcium carbonate (GCC) and pulp/GCC suspension. Comparison was made with two traditional cationic polymers used in wet end chemistry (poly-diallyldimethyl-ammonium chloride (PDADMAC) and poly-ethylene imine (PEI)). Flocculation efficiency was evaluated by flocculation parameters (mean floc size and number of counts) and by floc behavior under shear conditions, using a focused beam reflectance measurement (FBRM) technique. Results indicated different behaviors between the three chitosans when they were used for the flocculation of GCC and pulp/GCC suspensions. Chitosans were found to be more efficient over PDADMAC and PEI for flocculating small particles of the GCC suspension, but less efficient for increasing floc sizes, regardless of their MW or CCD. Flocculation parameters for pulp/GCC suspensions suggested the flocculation behavior of chitosan was close to that of PEI, but chitosan had higher efficiency and affinity towards cellulose fibers.

*Keywords:* Flocculation; Chitosan; Wet end additive; FBRM; Molecular weight; Charge density

*Contact information:* a: Department of Natural and Synthetic Polymers, Faculty of Chemical Engineering and Environmental Protection, "Gheorghe Asachi" Technical University of Iasi, Prof. Dr. Doc. Dimitrie Mangeron 73, Iasi, 700050, Romania; b: Department of Chemical Engineering, Faculty of Chemistry, Complutense University of Madrid, Av. Complutense s/n, 28040 Madrid, Spain;

\* Corresponding author: [elbo@tuiasi.ro](mailto:elbo@tuiasi.ro)

### INTRODUCTION

High retention efficiency during the formation of paper is very important to the efficiency of papermaking systems due to its large influence on both paper machine operations, as well as on the finished product quality. The usage of polymer retention aids is the most effective way to improve the retention of fine matter (cellulose fines and filler particles) during this process.

Generally, retention aids are high or medium molecular weight synthetic polymers, with a cationic, anionic, or nonionic charge. They can be used alone or in combination with other components (Hubbe *et al.* 2009; Zakrajsek *et al.* 2009). Conventional polyethylene amines, polyamides, polyacrylamides, *etc.*, are frequently used in combination with an inorganic or organic coagulant (Covarrubias *et al.* 2003). Though, each of these polymers has a clear and beneficial role in papermaking, some concerns about their environmental impact need to be taken into account, since they are obtained from fossil resources and are not easily biodegradable (Hubbe 2001; Cadotte *et al.* 2007). Thus, biodegradable polymers obtained from renewable resources have received increasing interest in the last years. Bio-based papermaking additives can be

produced from starch, chitosan, phosphate-modified glucomannan or by grafting acrylamide onto natural polysaccharides (Bratskaya *et al.* 2004; Kuutti *et al.* 2011).

Chitosan is a natural hetero-polymer containing both glucosamine and acetylglucosamine units, with a unique set of properties such as: natural cationic charge density, biodegradability, biocompatibility, non-toxicity, and antimicrobial activity (Crini and Badot 2008). These specific properties make it suitable for a large range of applications, including coagulation-flocculation processes (Bratskaya *et al.* 2004; Zemmouri *et al.* 2011). Chitosan has been used as an effective coagulant or flocculant for a wide variety of suspended solids in various food and fish processing industries (Fernandez and Fox 1997; Guerrero *et al.* 1998), as well as for suspensions of mineral colloids in water such as montmorillonite, bentonite, and kaolinite (Huang *et al.* 2000; Divakaran and Pillai 2002; Roussy *et al.* 2004; Chatterjee *et al.* 2009). At present, there are only a few applications of chitosan in papermaking, mainly focused on surface treatments in the production of specialty paper grades (Kuusipalo *et al.* 2005; Fernandes *et al.* 2009; Bordenave *et al.* 2010; Reis *et al.* 2011). Several studies deal with the use of chitosan to improve the wet and dry strength of paper (Laleg and Pikilikn 1992; Laleg 2001; Nada *et al.* 2006; Jahan *et al.* 2009). There are few studies on wet end applications of chitosan, which report on its effectiveness in anionic charge neutralization and retention/drainage improvements, simultaneously with an increase of paper strength (Bobu *et al.* 2002, Weis 2006; Nicu *et al.* 2011). However, these studies are concerning the effects of chitosan on wet end processes and paper properties under specific experimental conditions (paper stock composition, chitosan characteristics). Therefore, deeper research is needed on flocculation behavior of chitosan to lay the groundwork for efficient exploitation of its multiple functions as a wet end additive.

Retention aids work by aggregating the fine particles to form flocs that are large enough to be retained within the fiber network or could be attached to fiber surfaces by attractive forces (Zakrajsek *et al.* 2009; Kuutti *et al.* 2011). Depending on the retention aids used, the aggregation of the particles can occur by charge neutralization, patching, bridging, or a complex flocculation mechanism (Cadotte *et al.* 2007; Hubbe *et al.* 2009). It is also well known that the size of flocs and their ability to resist shearing forces are the main issues influencing basic wet end processes: retention, drainage, and formation (Fuente *et al.* 2003). Starting from this background, the objective of this work is to analyze in depth the flocculation behavior of the chitosan as a wet end additive and to compare its efficiency with that of conventional chemicals. Three chitosans with different molecular weights and cationic charge densities were investigated on two systems: calcium carbonate (GCC) and pulp/GCC suspension. Comparison was made with two high cationic density polymers used in wet end chemistry: poly-diallyldimethylammonium chloride (PDADMAC) and poly-ethylene imine (PEI). Flocculation efficiency was characterized by mean flocs size and number of counts, as well as by flocs behavior under shear, using a focused beam reflectance measurement (FBRM) technique.

## EXPERIMENTAL

### Materials

#### *Papermaking materials*

Ground calcium carbonate (GCC) suspension was prepared from Hydrocarb CL, a GCC supplied by OMYA (Spain), with the following characteristics:  $\text{CaCO}_3 > 98.5\%$ ,

mean diameter: 1.8  $\mu\text{m}$  (30% of the particles < 1  $\mu\text{m}$ ). A 0.2% suspension of GCC in distilled water was used in all experiments. Bleached eucalyptus pulp (total chlorine free, supplied by ENCE-Spain) was used to produce the pulp/GCC suspension. The suspension was prepared by soaking and disintegration of dried pulp in tap water at 2.5% consistency, followed by addition of 20% GCC related to dry fiber weight, homogenization, and then dilution of the pulp/GCC suspension to 1%. The main characteristics of the tap water used for pulp samples disintegrating are: pH 7.6; conductivity: 140  $\mu\text{S}/\text{cm}$ ; hardness: 60 ppm  $\text{CaCO}_3$ ; total alkalinity: 90 ppm  $\text{CaCO}_3$ ; sulphates: 30 ppm, and chlorides: 4.5 ppm.

#### *Flocculation additives*

Three types of chitosan, with different molecular weight (MW) and cationic charge density (CCD), were studied and compared with two common papermaking additives – PDADMAC and PEI. Chitosan samples were supplied by Sigma-Aldrich Co. The PDADMAC, supplied by BTG Instruments GmbH, has a low molecular weight and a high cationic charge density. The PEI (Polymin SK), supplied by BASF, is a medium to high molecular weight polymer with medium CCD. Chitosan was used as 1 g/L solution prepared in 0.1 M acetic acid, while PDADMAC and PEI were prepared in distilled water with 0.3935 g/L and 1 g/L concentrations, respectively. Table 1 shows the main characteristics of the polymers.

**Table 1.** Main Characteristics of Cationic Polymers

Polymer name	Polymer symbol	MW, kDa	CCD*, meq/g	Deacetylation degree, %
Chitosan - low MW	Ch.LMW	77	5.4	85.7
Chitosan - medium MW	Ch.MMW	293	5.8	86.5
Chitosan - high MW	Ch.HMW	444	3.8	87.5
Poly-diallyldimethylammonium chloride	PDADMAC	147	6.6	-
Poly-ethylenimine	PEI	1600	4.3	-

\*Measured by colloidal titration

## Methods and Procedures

#### *FBRM methodology*

The measurements were performed using a commercially available focused beam reflectance measurement system M500L, supplied by Mettler Toledo (U.S.A.). The FBRM (Focused Beam Reflectance Measurement) technique measures in real time the chord length distribution of particles in the suspension. Changes in the chord length with time make it possible to monitor flocculation, deflocculation, and reflocculation processes. The data can be used to analyze the flocs properties and the flocculation mechanisms (Blanco *et al.* 2002a; Ravnjak *et al.* 2006). The probe measures thousands of particles per second, obtaining a representative sample of the particles population in a short time (Fuente *et al.* 2003). Each measured particle chord length is named as a count. The measurement duration was selected to be 5s, which is fast enough to monitor the kinetics of the flocculation, deflocculation, and reflocculation processes, while maintaining the accuracy and a minimum ground signal in the measurement. In this

study, the mean chord size ( $\mu\text{m}$ ) and the total number of counts ( $\#/s$ ), both for the range 1-1000  $\mu\text{m}$ , were selected as the main statistic parameters to monitor the flocculation evolution with time. In addition, the number of counts ( $\#/s$ ) in different size ranges from 1 to 1000  $\mu\text{m}$  was used as complementary statistics (Blanco *et al.* 2002a; Ravnjak *et al.* 2006).

#### *Procedures for flocculation studies*

*Optimal polymer dosage:* In the first phase of this study, the optimal dosage of each polymer was determined. For these measurements, the FBRM probe was placed into 250 mL of sample. After 2 min. of stirring, the polymer was added in consecutive steps (0.25 mg/g GCC or pulp/GCC dry matter) at 30 s intervals, for all the polymers. To maintain the suspension homogeneity, while avoiding the disintegration of flocs, the suspension was stirred at 250 rpm in the case of GCC suspension and at 400 rpm for the pulp/GCC suspension. The optimal dosage corresponds to the slope change of the mean chord evolution curve. This dosage is determined graphically as the intersection between the straight lines representing the two slopes of the flocculation curve. It was defined as the dosage required for obtaining a maximum aggregation level, corresponding to the point at which the mean chord size is not changing significantly or even decreases with further polymer additions (Blanco *et al.* 2002b).

*Flocculation with different polymers:* Flocculation studies to compare the behaviour of the different products were carried at the optimal dosage of each product, when considered one at a time.

#### *Procedure for flocculation - deflocculation - reflocculation studies*

To determine floc properties and their behavior in relation with shear forces, the optimal dosage of polymer was added to the suspension while stirring and homogenization at low speed (250 rpm for 0.2% GCC suspension and 400 rpm for 1% pulp/GCC suspension), and the conditions in the system were allowed to evolve for 5 min. In the deflocculation phase, the stirring speed was increased to 750 rpm for GCC suspension and 800 rpm for pulp/GCC suspension, and maintained for 5 min. Finally in the reflocculation phase, the stirring speed was reduced to the initial value for another 5 min or until stabilization of the mean chord size was achieved, to evaluate the reflocculation capacity of broken flocs. For the deflocculation-reflocculation studies, the stirring speed was established considering the previous studies in this field (Blanco *et al.* 2002a; Blanco *et al.* 2005; Fuente *et al.* 2005; Ravnjak *et al.* 2006), where it was chosen to reproduce different levels of hydrodynamic forces existing during the papermaking process: a high level of shear forces to produce deflocculation (like in fine sorting plant) and a low level of shear forces to allow reflocculation (like in the forming zone of paper machine wire).

#### *Calculation of deflocculation - reflocculation indexes*

Deflocculation and reflocculation indexes are used to characterize the stability of flocs subjected to strong shear forces, and the ability of flocs to recover after shear ends. The two indexes are calculated using the following equations,

$$\text{Deflocculation index (\%)} = \frac{y_4 - y_3}{y_3 - y_1} \cdot 100 \quad (1)$$

$$\text{Reflocculation index (\%)} = \frac{y_5 - y_4}{y_3 - y_1} \cdot 100 \quad (2)$$

where  $y_1$  is the mean chord size before polymer addition;  $y_3$  is the mean chord size after polymer addition and before shear forces increases;  $y_4$  is the minimum of the mean chord size under strong shear forces; and  $y_5$  is the maximum of the mean chord size after strong shear forces ends (see Fig. 1).

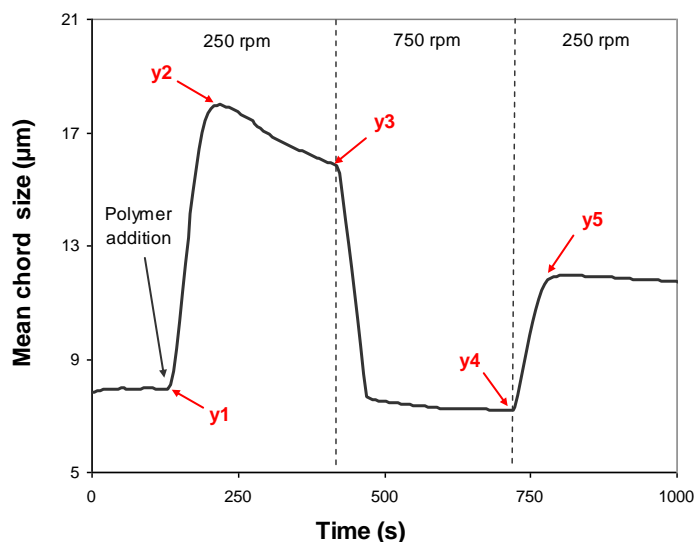


Fig. 1. Definition of terms used in the calculation of deflocculation and reflocculation indexes

## RESULTS AND DISCUSSION

### Optimal Polymer Dosage

The optimal polymer dosages were obtained from the graphs of Figs. 2 and 3. Table 2 summarizes the optimal dosage of each polymer for both GCC suspension and GCC/pulp suspension.

The flocculation curves for GCC suspension (Fig. 2) were very similar for all the polymers, but the optimal dosages for PDAMAC and PEI were lower compared to those of the chitosans. Molecular weight had an important influence on the optimal dosage of the chitosans: higher molecular weights decreased the optimal dosage. This suggested that the flocculation started at high polymer coverage rate of GCC particles and a multilayer adsorption of chitosan is also possible. The medium MW chitosan showed similar behavior to that of PEI, which is postulated to develop flocculation by a bridging mechanism. Low MW chitosan produced small flocs, very similar to those of PDADMAC, suggesting a charge neutralization flocculation. High MW chitosan showed an intermediate efficiency in increasing flocs size. The effect could be due to the polymeric chain conformation. Medium molecular weight chitosan (ChMMW) with high cationic density could adopt a flatter conformation on the particle, which results in the formation of cationic patches that attract the polymer free surfaces of other particles and thus leading to lower number of flocs but with higher size. In contrast, HMW chitosan

with higher molecular weight and low density of cationic charges could adopt a semi-flexible-coil model and form many loops that absorb GCC particles, leading to higher number of counts but lower mean chord size (Blanco *et al.* 2002b).

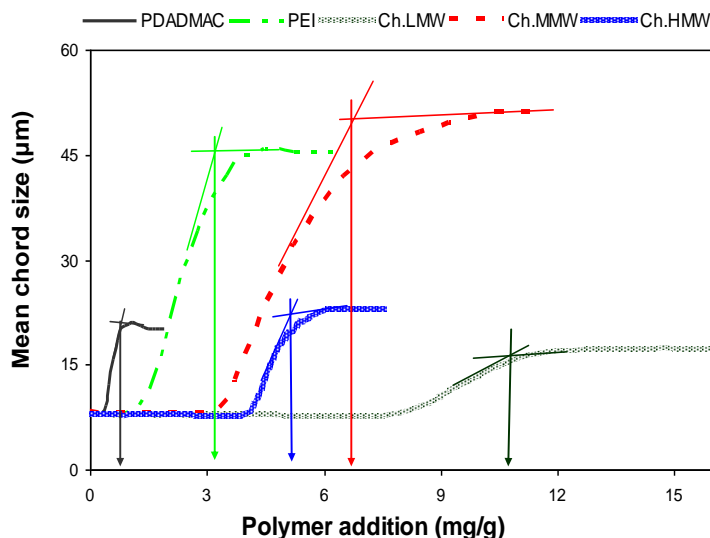


Fig. 2. GCC suspension: optimal polymer dosage

In the presence of cellulose fibers (pulp/GCC suspension), flocculation exhibited a distinct shape (Fig. 3), indicating that different and more complex interactions are taking place. The efficiency of the polymers appeared to be influenced by the interaction intensity between each polymer with the cellulose fibers and the calcium carbonate particles, respectively. Therefore, an important reduction of optimal dosage for all chitosans, regardless of their MW and/or CCD, is achieved (see Table 2), which indicated a strong interaction and a specific affinity between chitosan molecules and cellulose fibers, more intense than for GCC particles.

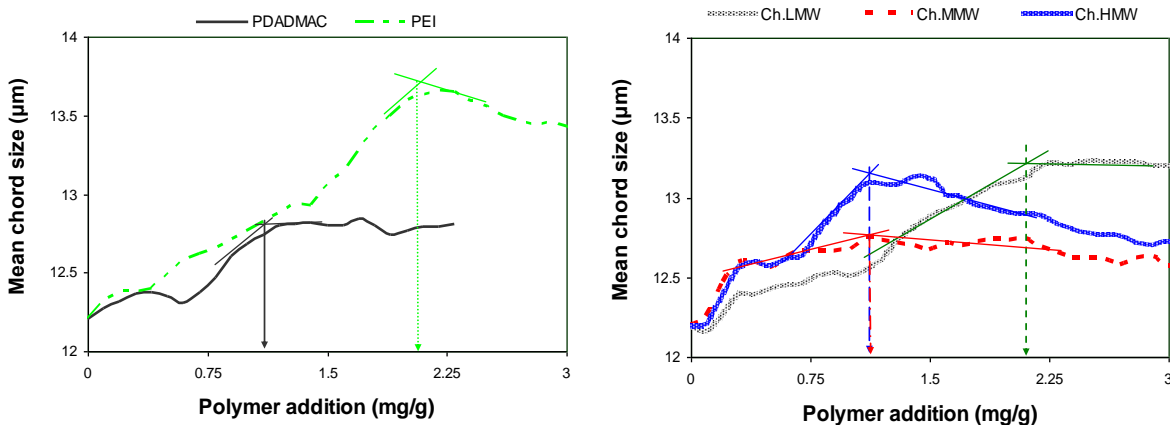


Fig. 3. Pulp/GCC suspension: Optimal polymer dosage

The absorption of chitosan on cellulose nanofibril model surfaces has been studied on a molecular level using the Quartz Crystal Microbalance with Dissipation (QCM-D) and Atomic Force Microscopy (AFM) techniques at different pH conditions

(Myllytie 2009). It was found that chitosan adsorbs on cellulose even in the absence of electrostatic attraction, demonstrating the specific interaction between these two polymers. Thus, it is possible that in the presence of cellulose fibers, chitosan is first adsorbed on fiber fines, creating cationic sites on which calcium carbonate particles are adsorbed, causing an increase in floc size. Unlike calcium carbonate suspension, there were no differences between polymers for the minimal dosage, the flocculation started at first addition (0.25 mg/g) for all polymers. This observation supports the previous hypothesis that the chitosan was adsorbed preferentially onto the cellulose fibers/fines.

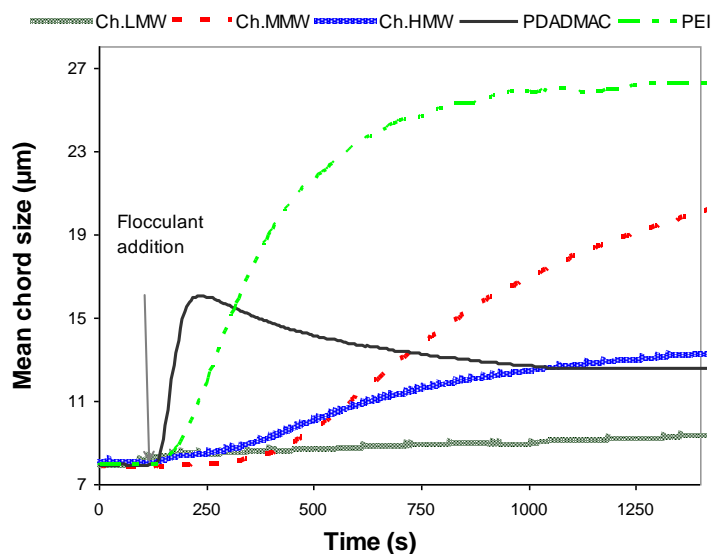
**Table 2.** Optimal Dosage of Polymer for GCC and GCC/Pulp Suspensions

Cationic polymer	Optimal dosage, mg/g		Change of optimal dosage, %
	GCC	Pulp/GCC	
Ch.LMW	10.8	2.1	- 80.5
Ch.MMW	6.5	1.1	- 83.1
Ch.HMW	5.0	1.1	- 78.4
PDADMAC	0.7	1.2	+ 71.4
PEI	3.3	2.1	- 35.4

## Flocculation of GCC Suspension

### *Flocculation kinetics*

Theoretically, when a polymer is added to a suspension, one observes that the particles start to aggregate, which results in an increase of the aggregate size (mean chord size,  $\mu\text{m}$ ) and a decrease of particles number (counts, #/s). In the case of GCC suspensions, both the mean chord size (Fig. 4) and the total number of counts (Fig. 5) increased at the same time. This apparent contradiction can be explained by the aggregation of small calcium carbonate particles (GCC contains 30% particles  $< 1 \mu\text{m}$ ), which are not detected and quantified by the FBRM device in the initial stage before polymer addition (Blanco *et al.* 2002b; Fuente *et al.* 2003). This is illustrated in Fig. 6a.



**Fig. 4.** GCC flocculation: Evolution of the mean chord size with the time

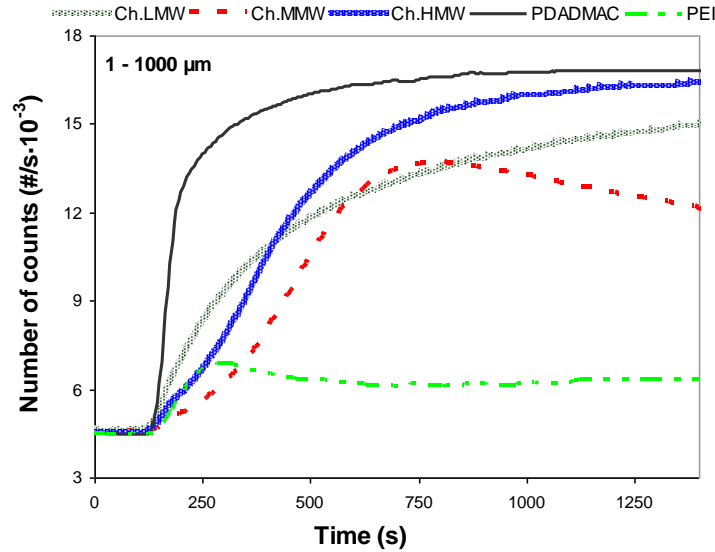


Fig. 5. GCC flocculation: Evolution of the total number of counts with the time

The evolution with time of the flocculation process was clearly different for the various polymers (Figs. 4 and 5). The PDADMAC caused a fast aggregation and achieved equilibrium very quickly as the mean chord size and the number of counts reached very fast a relatively constant value. While the final value of the mean floc size is relatively small, the value of the total number of counts is high (Fig. 5). The PEI also induced a fast aggregation, but with a much higher mean floc size, a lower number of counts, and a slower and less defined equilibrium.

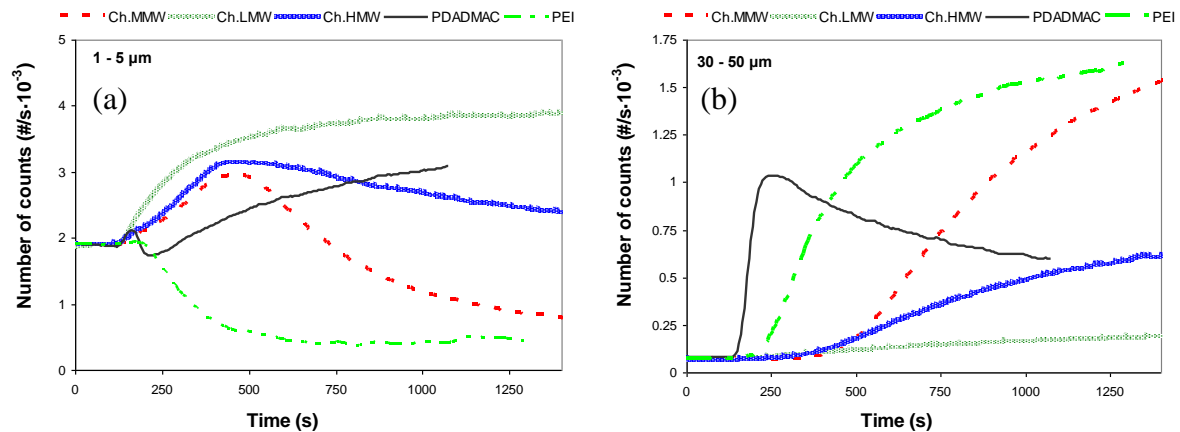


Fig. 6. GCC flocculation: Evolution of the number of counts with the time: a) 1-5  $\mu\text{m}$ ; b) 30-50  $\mu\text{m}$

The flocculation induced by the chitosans differed from those of the PDADMAC and PEI in two aspects. First, the floc size increased much more slowly than those with PDADMAC and PEI, and none of the chitosans reached a stable equilibrium (Fig. 4). Second, the number of flocs increased faster than those with PDADMAC and PEI, and the flocculation curve showed stabilization at a much longer time (Fig. 5). Among the chitosans, the medium molecular chitosan (Ch.MMW) was the one yielding the largest flocs and the clearest stabilization of the number of flocs. All chitosans were efficient in

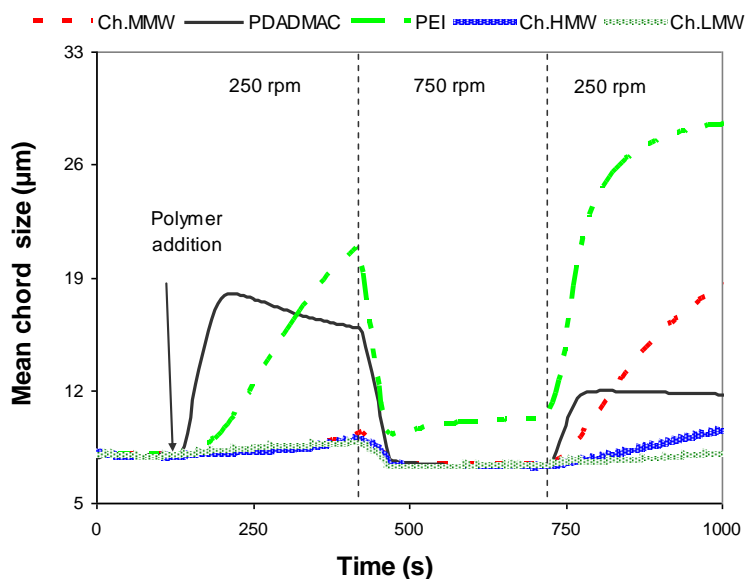


the flocculation of small particles (Fig. 6). In the 1-5  $\mu\text{m}$  chord size range, the Ch.LMW was more efficient than the others, while Ch.MMW performed better in the 30-50  $\mu\text{m}$  chord size range. Figure 6 also showed the medium molecular chitosan behavior is more similar to that of the PEI, which is in agreement with the mean chord size evolution with polymer dosage (Fig. 2).

#### *Floc behavior under shear forces*

Figure 7 shows the evolution of the mean chord size during the three consecutive phases under different shearing forces: 1) low (250 rpm), 2) high (750 rpm), and 3) low (250 rpm). Figure 8 shows the calculated deflocculation and reflocculation indexes (DI and RI).

When the flocs were subjected to high shear rates, the mean chord size was abruptly reduced for the PEI and PDADMAC; this decrease was slightly less pronounced for the chitosans (Fig. 7). This observation was also confirmed by the negative values of the deflocculation indexes (Fig. 8), which characterize the resistance of flocs to shear action. When the shear forces returned back to the initial value (250 rpm), the flocs recovered, regardless the polymer type (the reflocculation index showed positive values for all polymers).

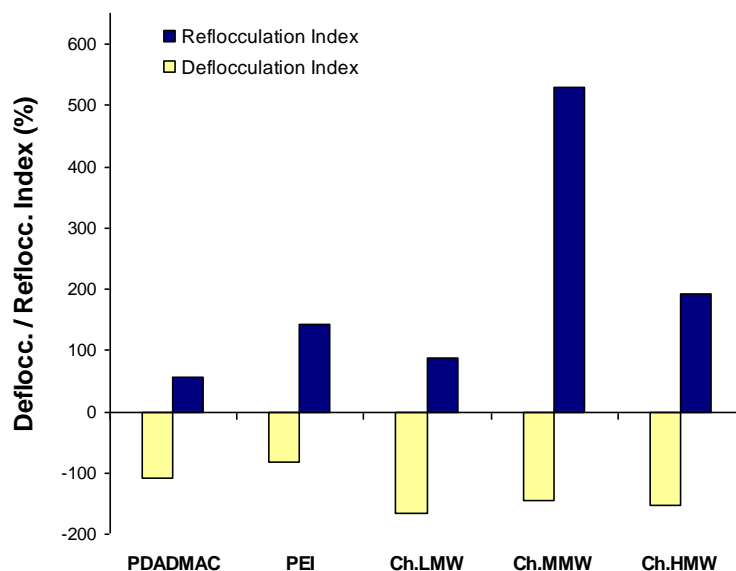


**Fig. 7.** GCC suspension: Influence of shearing forces on mean floc size evolution

The deflocculation-reflocculation processes were strongly influenced by polymer type. The PDADMAC formed flocs with low resistance to shear forces (100% DI) that are recovered in a very short time, but at low recovering rate (RI: 57%). This behavior, coupled with flocculation parameters (Figs. 4 and 5), showed that PDADMAC works by a patch flocculation mechanism on the GCC suspension. The PEI formed the largest flocs with a relative high resistance to shear forces (80% DI), which were easily recovered (*i.e.*, RI higher than 100%). These deflocculation-reflocculation indexes, correlated with flocculation parameters (Figs. 4 and 5), which indicated that PEI works by a complex aggregation mechanism. This mechanism could involve a fast aggregation of small particles in the first step, followed by bridge flocculation in a second step, which results

in large-sized flocs. Unlike other high MW polymers, PEI showed not only the capacity to reflocculate the broken flocs under high shear forces, but also to form larger flocs than before. This behavior could be attributed to its branched structure and relatively high cationic density (Rasteiro *et al.* 2008a,b).

All chitosans developed flocs with low shear resistance. The values of the DI (Fig. 8) were higher than 100%, which indicated that all chitosans initially dispersed the aggregates. The dispersing effect could be explained by the higher optimal dosages of the chitosans compared to PDADMAC and PEI (Table 2). It is possible that the chitosan is adsorbed as multi-layers on the GCC particles, which leads to an excess of polymer that is brought into suspension medium when subjected to intense shear forces. Otherwise, the deflocculation index (DI) was correlated with optimal dosage, in the following order: Ch.LMW>Ch.HMW>Ch.MMW. The reflocculation index had a reverse order: Ch.LMW<Ch.HMW<Ch.MMW. Low molecular weight chitosan appeared to behave similarly to PDADMAC, by a charge neutralization mechanism, while Ch.HMW and Ch.MMW, behaved more like PEI, by combining charge neutralization and a bridging mechanism.



**Fig. 8.** GCC suspension: Deflocculation and reflocculation indexes for the polymers studied

The flocculation kinetics of GCC suspension with chitosan was influenced by both molecular weight and cationic charge density, but molecular weight seemed to be the more important factor. This result was in agreement with recent patents regarding the adsorption of polysaccharides onto mineral surfaces, which demonstrated that the molecular weight of the flocculant was the most critical characteristic (Likitalo and Käksi 2005; Kuutti *et al.* 2011).

## Flocculation of Pulp/GCC Suspension

### *Flocculation kinetics*

The evolution of the mean chord size and the number of counts in time, at the optimal dosage for each polymer (see Table 2), are graphically represented in Figs. 9 and 10, respectively.

The shape of the flocculation curves of the pulp/GCC suspension (Fig. 9) were completely different than the shape exhibited by the GCC suspension (see Fig. 4). In the case of GCC suspension, the PDADMAC produced a fast increase of floc size to maximum values, which then was stabilized at lower value. On the contrary, the PEI and chitosans showed a slower increase and a stabilization of floc size to the highest value. In the case of pulp/GCC suspension, the PDADMAC appeared totally ineffective in the flocculation of fines materials (no increase of floc size). In contrast, the size of flocs produced by the PEI and chitosans increased fast to a maximum value and then stabilized at lower value.

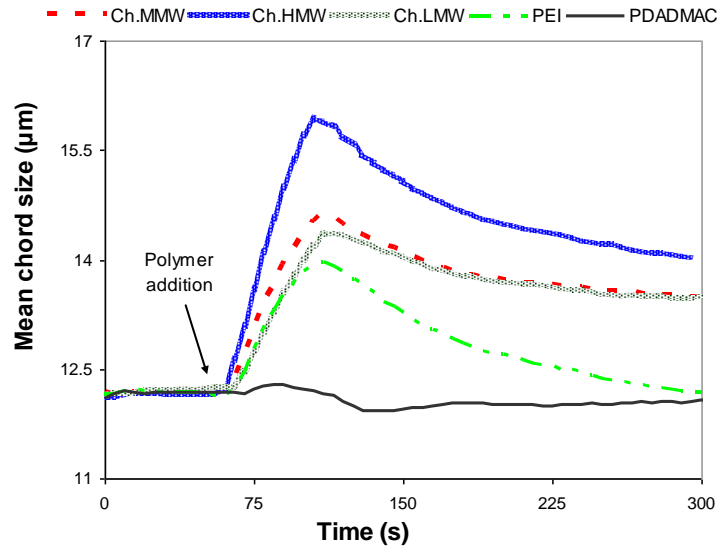


Fig. 9. Pulp/GCC flocculation: Evolution of mean chord size with the time

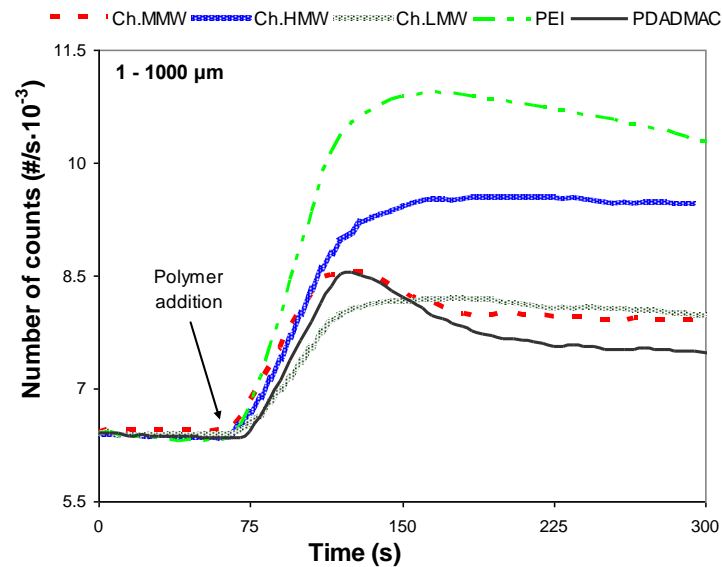


Fig. 10. Pulp/GCC flocculation: Evolution of the total number of counts with the time

The flocculation with PEI did not reach a clear equilibrium since the flocculation rate decreased continuously with stirring time. In the case of the chitosans, the mean floc size was stabilized at about half of the maximum chord size reached. Unlike the mean chord size, the number of counts with time reached a clear equilibrium at about 100 s after polymer addition (Fig. 10). This equilibrium could be correlated, to a certain extent, with the mean chord size evolution, which started to decrease after 40 s, leading to an increase in the number of particles until mean chord size stabilized.

Total number of counts increased for all polymers, similar to GCC flocculation, which indicated the flocculation of small particles, and possibly the coagulation of colloidal and dissolved material from pulp suspension. However, the efficiency of polymers in the presence of cellulose fibers was totally different from that of GCC suspension (see Fig. 5). In the case of GCC suspension, PDADMAC was the most and PEI was the least efficient product; chitosans were in between. In the case of pulp/GCC suspension, PEI and Ch.HMW were the most efficient products at increasing the total number of counts. The other two chitosans exhibited similar efficiency as PDADMAC.

As a conclusion, chitosans and PEI exhibit similar behavior in flocculation of pulp/GCC suspension; however, the chitosans have a higher efficiency in terms of increasing floc size (Fig. 9), but a lower efficiency at increasing the number of counts (Fig. 10). Chitosan efficiency increased in parallel to the increase of its molecular weight. Although the maximum value for counts number was lower than for GCC suspension, the chitosans showed higher efficiency in aggregating small particles in pulp/GCC suspension than GCC suspension, which has been demonstrated by the lower time needed to reach stabilization (75 s for pulp/GCC suspension and 600 s for GCC suspension). This could be explained by the high affinity of chitosan for cellulosic fibers, which reduces the amount of polymer to be adsorbed on the surface of small particles. Generally, cellulosic fibers are naturally anionic in charge and cationic polymers are readily adsorbed onto fibers, mainly by electrostatic attraction (Myllytie *et al.* 2009). However, a non-electrostatic interaction for adsorption of chitosan on cellulosic fibers, specific for polysaccharides, has been also suggested. For example, plausible interactions of chitosan with cellulose fiber surface are hydrogen bond forming or/and chemical reactions, which could enhance the adsorption of chitosan onto cellulose in the absence of electrostatic attraction (Myllytie 2009; Saarinen *et al.* 2009). Thus, these possible interactions between the reactive groups of chitosan and cellulose could explain the significant differences between its flocculation behavior in GCC suspension and pulp/GCC suspension.

#### *Floc behavior under shear forces*

When cellulosic fibers are present in the suspension, the deflocculation-reflocculation processes changed significantly when compared to GCC suspension. The mean chord size decreased for all polymers when shear rates increased at 800 rpm (Fig. 11); however, floc resistance, quantified by the values of deflocculation index (DI), differed substantially (Fig. 12). Opposite to the GCC suspension, in which the PEI and PDADMAC developed more resistant flocs (low DI), the chitosans produced more stable and resistant flocs in the pulp/GCC suspension. No significant differences were observed with the three types of chitosan regarding their stability under strong shear forces.

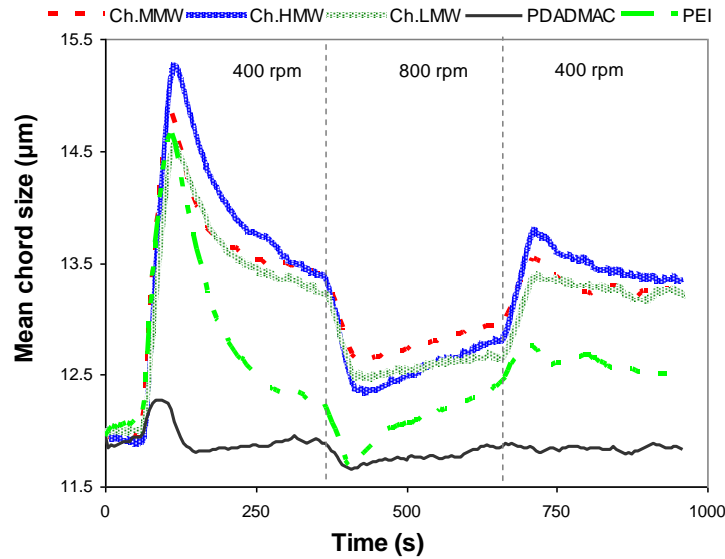


Fig. 11. Pulp/GCC suspension: Influence of shearing forces on mean floc size evolution

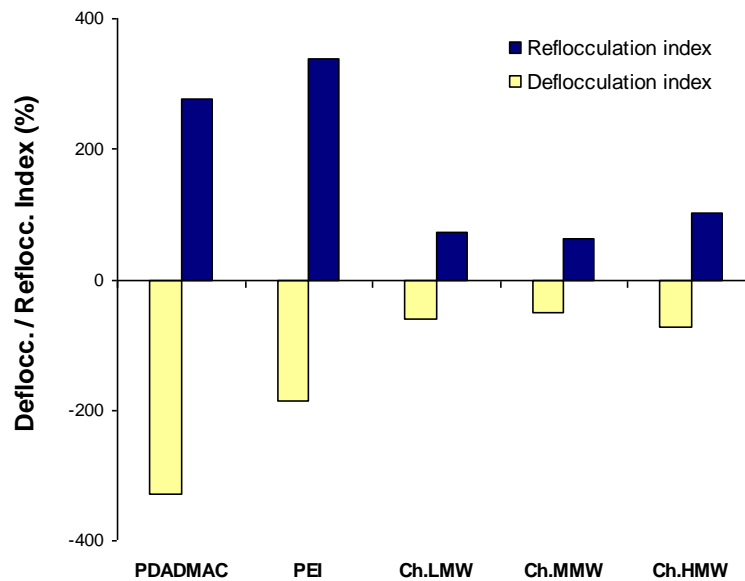


Fig. 12. Deflocculation and reflocculation indexes for the polymers studied

After the shear forces decreased (400 rpm), only 84% of initial floc size was recovered for the PDADMAC flocculation, while the recovery was higher than 100% for the PEI (about 180%) and chitosans (120%, 122%, and 138% in the order of molecular weight increase, respectively). The characteristics of the deflocculation-reflocculation processes confirmed the particular behavior of the chitosan in the presence of cellulose fibers, as evidenced by the flocculation kinetics. The low values of the deflocculation index and high values of the reflocculation index demonstrated again the strong interaction of chitosan with the cellulose fibers, which resulted in a stable and reversible flocculation mechanism. This hypothesis is also supported by the observation that there were no significant differences among them due to their molecular weight and/or cationic charge density.

## CONCLUSIONS

### 1. Flocculation of GCC Suspension

All chitosans were efficient for the flocculation of small GCC particles ( $<1\mu\text{m}$ ), as demonstrated by the rapid increase of the number of flocs and a very slow increase of the mean floc size; the flocculation curve (evolution of mean floc size with time) did clearly denote a stabilized equilibrium. This behavior cannot be correlated with either their MW or CCD. The flocculation parameters differed substantially from those of PDADMAC, which produced small flocs with fast stabilization, and PEI, which formed large flocs with slow stabilization time.

The study on the deflocculation-reflocculation processes showed that all the chitosans formed flocs with low resistance to shear forces (high deflocculation index), which reflocculate slowly and at different reflocculation rates depending on the both MW and CCD. Low MW chitosan with high CCD behaves similar to PDADMAC, by a charge neutralization mechanism. The high MW chitosan with medium CCD and the medium MW chitosan (with higher MW and similar CCD as low MW chitosan), behaved similar to PEI, by a combination of charge neutralization and a bridging mechanism.

### 2. Flocculation of Pulp/GCC Suspension

In the presence of cellulose fibers, the flocculation behavior of all polymers, and in particular the chitosans, was completely different to that of the GCC suspension. All the chitosans behaved similar to the PEI; however, the chitosans had higher flocculation efficiency in terms of mean floc size and a lower efficiency in terms of number of flocs. These flocculation parameters are mainly influenced by the molecular weight of chitosan, the highest values being obtained by the high MW chitosan. Although, the maximum value for counts number was lower than for GCC suspension, the chitosans showed higher efficiency in aggregating small particles in pulp/GCC suspension than GCC suspension, which has been proved by the lower time needed to reach stabilization (75 s for pulp/GCC suspension and 600 s for GCC suspension). This could be explained by high affinity of chitosan for cellulosic fibers, which reduces the amount of polymer to be adsorbed on the surface of small particles.

The analysis of the deflocculation-reflocculation processes confirmed the particular behavior of the chitosan in the presence of cellulose fibers. Comparatively with the GCC suspension, the resistance of the flocs to shear action (deflocculation index) increased substantially, regardless of the chitosans' characteristics. On the other hand, the floc size recovery rate increased with the molecular weight of the chitosan. The reflocculation indexes were higher than 100%, which demonstrated the high potential of the chitosan to recover and even to increase the floc size after high shear ends.

Although the flocculation parameters (mean chord size and counts number) suggested the flocculation behavior of chitosan was close to that of PEI, the deflocculation-reflocculation indexes showed a clear difference in the flocculation mechanism due to the particular affinity of chitosan for cellulose fibers. Otherwise, possible interactions between the reactive groups of chitosan and cellulose were probable and could explain the huge difference between its flocculation behavior with GCC suspension and pulp/GCC suspension.

## ACKNOWLEDGMENTS

This paper was supported by the project PERFORM-ERA "Postdoctoral Performance for Integration in the European Research Area" (ID-57649), financed by the European Social Fund and the Romanian Government, and by the project PROLIPAPPEL II (P2009/AMB-1480) from the Community of Madrid in Spain.

## REFERENCES CITED

- Blanco, A., Fuente, E., Negro, C., Monte, C., and Tijero, J. (2002.a). "Focused beam reflectance measurement as a tool to measure flocculation," *TAPPI J.* 1(10), 14-20.
- Blanco, A., Fuente, E., Negro, C., and Tijero, J. (2002.b). "Flocculation monitoring: Focused beam reflectance measurement as a measurement tool," *Can. J. Chem. Eng.* 80(4), 734-740.
- Blanco, A., Negro, C., Fuente, E., and Tijero, J. (2005). "Effect of shearing forces and flocculant overdose on filler flocculation mechanisms and floc properties," *Ind. Eng. Chem. Res.* 44(24), 9105-9112.
- Bobu, E., Ciolacu, F., and Anghel, A. (2002). "Prevention of colloidal material accumulation in short circulation of paper machine," *Wochenblatt fur Papierfabrikation* 130(9), 576-583.
- Bordenave, N., Grelier, S., and Coma, V. (2010). "Hydrophobization and antimicrobial activity of chitosan and paper-based packaging material," *Biomacromolecules* 11(1), 88-96.
- Bratskaya, S., Schwarz, S., and Chervonetsky, D. (2004). "Comparative study of humic acids flocculation with chitosan hydrochloride and chitosan glutamate," *Water Res.* 38(12), 2955-2961.
- Cadotte, M., Tellier, M. E., Blanco, A., Fuente, E., van de Ven, T. G. M., and Paris, J. (2007). "Flocculation, retention and drainage in papermaking: a comparative study of polymeric additives," *Can. J. Chem. Eng.* 85(2), 240-248.
- Chatterjee, T., Chatterjee, S., and Han Woo, S. (2009). "Enhanced coagulation of bentonite particles in water by a modified chitosan biopolymer," *Chem. Eng. J.* 148(2-3), 414-419.
- Covarrubias, R. M., Kessler, B., and Magee, K. (2003). "Nanotechnology in practice: Improving machine performance in a newsprint mill," In: *2003 TAPPI Spring Technical Conference & Trade Fair*, TAPPI Press, Atlanta, GA.
- Crini, G., and Badot, P. M. (2008). "Application of chitosan, a natural amino-polysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature," *Prog. Polym. Sci.* 33(4), 399-447.
- Divakaran, R., and Pillai, V.N.S. (2002). "Flocculation of river silt using chitosan," *Water Res.* 36(9), 2414-2418.
- Fernandez, M., and Fox, P. F. (1997). "Fractionation of cheese nitrogen using chitosan," *Food Chem.* 58(4), 319-322.
- Fuente, E., Blanco, A., Negro, C., San Pio, I., and Tijero, J. (2003). "Monitoring flocculation of fillers in papermaking," *Paper Technol.* 44(8), 41-50.
- Guerrero, L., Omil, F., Mendez, R., and Lema, J. M. (1998). "Protein recovery during the overall treatment of wastewaters from fish-meal factories," *Bioresour. Technol.* 63(3), 221-229.

- Huang, C. P., Chen, S. C., and Pan, J. R. S. (2000). "Optimal condition for modification of chitosan: A biopolymer for coagulation of colloidal particles," *Water Res.* 34(3), 1057-1062.
- Hubbe, M.A. (2001). "Wet-end chemistry: Feature essay," [www.ncsu.edu/~hubbe/new/goodchem](http://www.ncsu.edu/~hubbe/new/goodchem)
- Hubbe, M. A., Nanko, H., and McNeal, M. R. (2009). "Retention aid polymer interactions with cellulosic surfaces and suspensions: A review," *BioResources* 4(2), 850-906.
- Jahan, M. S., Noori, A., Ahsan, L., Chowdhury, D. A. N., and Quaiyyum, M. A. (2009). "Effects of chitosan as dry and wet strength additive in bamboo and acacia pulp," *IPPTA Journal* 21(2), 85-92.
- Kuusipalo, J., Kaunisto, M., Laine, A., and Kellomäki, M. (2005). "Chitosan as a coating additive in paper and paperboard," *TAPPI J.* 4(8), 17-21.
- Kuutti, L., Haavisto, S., Hyvärinen, S., Mikkonen, H., Koski, R., Peltonen, S., Suortti, T., and Kyllönen, H. (2011). "Properties and flocculation efficiency of cationized biopolymers and their applicability in papermaking and in conditioning of pulp and paper sludge," *BioResources* 6(3), 2836-2850.
- Laleg, M., and Pikilik, I. (1992). "Strengthening of mechanical pulp webs by chitosan," *Nord. Pulp Pap. Res. J.* 7(4), 174-180.
- Laleg, M. (2001). "Surface sizing with chitosan and chitosan blends," In: *87<sup>th</sup> Annual Meeting*, PAPTAC, Montreal, PQ, Canada.
- Likitalo, A., and Käki, J. (2005). "Method for manufacturing high-cationic starch solutions," US Patent 6855819.
- Myllytie, P. (2009). "Interactions of polymers with fibrillar structure of cellulose fibers: A new approach to bonding and strength in paper," *Doctoral Thesis*, Helsinki University of Technology, Espoo, Finland.
- Myllytie, P., Salmi, J., and Laine, J. (2009). "The influence of pH on the adsorption and interaction of chitosan with cellulose," *BioResources* 4(4), 1647-1662.
- Nada, A. M. A., El-Sakhawy, M., Kamel, S., Eid, M. A. M., and Adel, A. M. (2006). "Mechanical and electrical properties of paper sheets treated with chitosan and its derivatives," *Carbohydr. Polym.* 63(1), 113-121.
- Nicu, R., Bobu, E., and Desbrieres, J. (2011). "Chitosan as cationic polyelectrolyte in wet-end papermaking system," *Cell. Chem. Technol.* 45(1-2), 105-111.
- Rasteiro, M. G., Garcia, F. A. P., Ferreira, P., Blanco, A., Negro, C., and Antunes, E. (2008a). "The use of LDS as a tool to evaluate flocculation mechanisms," *Chem. Eng. Process.* 47(8), 1323-1332.
- Rasteiro, M. G., Garcia, F. A. P., Ferreira, P., Blanco, A., Negro, C., and Antunes, E. (2008b). "Evaluation of flocs resistance and reflocculation capacity using the LDS technique," *Powder Technol.* 183(2), 231-238.
- Ravnjak, D., Fuente, E., Negro, C., and Blanco, A. (2006). "Flocculation of pulp fractions induced by fluorescently-labeled PDADMAC," *Cell. Chem. Technol.* 40(1-2), 77-85.
- Reis, A. B., Yoshida, C. M. P., Reis, A. P. C., and Franco, T. T. (2011). "Application of chitosan emulsion as a coating on kraft paper," *Polym. Int.* 60(6), 963-969.
- Roussy, J., Vooren, M. V., and Guibal, E. (2004). "Chitosan for the coagulation and flocculation of mineral colloids," *J. Disp. Sci. Technol.* 25(5), 663-677.
- Saarinen, T., Österberg, M., and Laine, J. (2009). "Properties of cationic polyelectrolyte layers adsorbed on silica and cellulose surfaces studied by QCM-D - Effect of



polyelectrolyte charge density and molecular weight,” *J. Disp. Sci. Technol.* 30(6), 969-979.

Weis, J. (2006). PTS News, No.05, Munich, Germany.

Zakrajsek, N., Fuente, E., Blanco, A., and Golob, J. (2009). “Influence of cationic starch adsorption on fibers flocculation,” *Chem. Eng. Technol.* 32(8), 1259-1265.

Zemmouri, H., Kadouche, S., Lounici, H., Hadioui, M., and Mameri, N. (2011). “Use of chitosan in coagulation flocculation of raw water of Keddara and Beni Amrane dams,” *Water Sci. Technol.: Water Supply* 11(2), 202-210.

Article submitted: October 1, 2012; Peer review completed: November 15, 2012; Revised version received and accepted: December 7, 2012; Published: December 17, 2012.