

Efficiency of Chitosan and their Combination with Bentonite as Retention Aids in Papermaking

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In a previous work (Nicu *et al.* 2013), the flocculation efficiency of three chitosans differing by molecular weight and charge density were evaluated for their potential use as wet end additives in papermaking. According to the promising results obtained, chitosan (single system) and its combination with bentonite (dual system) were evaluated as retention aids, and their efficiency was compared with poly(diallyl dimethyl ammonium chloride) (PDADMAC) and polyethylenimine (PEI). In single systems, chitosan was clearly more efficient in drainage rate than PDADMAC and PEI, especially those with the lowest molecular weights; however, retention is considerably lower. This drawback can be overcome by using dual systems with anionic bentonite microparticles, with the optimum ratio of polymer:bentonite being 1:4 (wt./wt.). In dual systems, the differences in retention were almost negligible, and the difference in drainage rate was even higher, together with better floc reversibility. The most efficient chitosan in single systems was Ch.MMW, while Ch.LMW was the most efficient in dual systems. The flocculation mechanism of chitosan was a combination of patch formation, charge neutralization, and partial bridge formation, and the predominant mechanism depended on the molecular weight and charge density of the chitosan.

Keywords: Chitosan; Bentonite; Flocculation; Retention aids; Retention; Drainage

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INTRODUCTION

High retention during paper formation is very important in papermaking systems due to the large influence on both paper machine performance and finished product quality. Low retention can lead to many problems, including poor runnability, increased deposits, sheet defects, higher additive costs, and increased downtime. On the other hand, drainage is a major factor in industrial operation as it is related to paper machine speed (and thus, the productivity) and energy consumption.

Papermakers use chemical additives to control the wet end processes, with sheet formation as the compromise between retention and drainage. These processes, as well as the paper characteristics, are influenced by the aggregation degree of paper stock components, which is mainly related to the characteristics of the additives and stock components used (Hubbe 2001). Retention aids are those chemicals added to retain colloidal-sized particles (such as cellulosic fine particles and fillers) in the thin mat of fibers during sheet formation (Li *et al.* 2004a). Typical retention systems are dual, with either dual polymer or microparticle systems. In dual polymer systems, a highly cationic polymer of low molecular weight is added, and an anionic (or cationic) polymer of high molecular

weight follows. In microparticle systems, a microparticle solid anionic flocculant such as silica or bentonite typically is added after a cationic flocculant of high molecular weight and medium charge density (Blanco *et al.* 2001). Retention additives are natural or synthetic polymers, the latter being the most frequently used. The natural polymers employed are typically cationic starch or carboxymethyl cellulose; commonly used synthetic polymers are poly-diallyl-dimethyl-ammonium chloride (PDADMAC), polyethylene imine (PEI), polyacrylamide, polyethylene oxide, *etc.* (Li *et al.* 2004a).

Synthetic polymers are efficient but poorly degradable in conventional water treatments, and they accumulate in water systems. Environmentally sustainable alternatives to these polymers, based on natural polymers, are of growing interest (Rojas-Reyna *et al.* 2010; Thakur *et al.* 2015; Thakur and Voicu 2016). Bio-based papermaking additives are produced from a variety of sources, and some of the most notable materials are chitosan, starch, phosphate-modified glucomannan, and natural polysaccharides grafted with acrylamide (Bratskaya *et al.* 2004; Kuutti *et al.* 2011). Among them, chitosan is probably the most promising cationic biopolymer for extensive application in flocculation applications (Bratskaya *et al.* 2004).

Chitosan is a polycationic, high molecular weight, linear copolymer of glucosamine and N-acetyl-glucosamine units. It also has a unique set of properties such as natural cationic charge density, biodegradability, biocompatibility, non-toxicity, and antimicrobial activity (Crini and Badot 2008; Renault *et al.* 2009; Thakur and Thakur 2014). These specific properties make it suitable for a large range of applications, including coagulation-flocculation processes (Bratskaya *et al.* 2004; Renault *et al.* 2009; Zemmouri *et al.* 2011; Miranda *et al.* 2013; Yang *et al.* 2016). The most relevant characteristics of chitosan in relation to flocculation are charge density (related to its deacetylation degree), molecular weight, and molecular structure (Renault *et al.* 2009; Thakur and Thakur 2014). The reactivity of chitosan for the coagulation and flocculation of suspended particles and colloids can result from several mechanisms. The most common mechanisms involved in chitosan flocculation are charge neutralization, adsorption (related to protonated amine groups), precipitative coagulation, bridge formation (related to the high molecular weight of biomacromolecules), and electrostatic patch. The flocculation mechanism also depends on different factors such as pH, ionic strength of the solution, and coagulant concentration (Chatterjee *et al.* 2009; Renault *et al.* 2009).

At present, there are only a few applications of chitosan in papermaking, mainly focusing on the surface treatments in the production of specialty paper grades (Kuusipalo *et al.* 2005; Bordenave *et al.* 2010; Reis *et al.* 2011), the improvement of the wet and dry strength of paper (Laleg 2001; Nada *et al.* 2006; Jahan *et al.* 2009; Chen *et al.* 2013), water treatment (Wang *et al.* 2009; Miranda *et al.* 2013), or its possible use in wet end applications as an anionic charge neutralization system (Bobu *et al.* 2002; Li *et al.* 2004b; Belosinschi and Bobu 2008; Nicu *et al.* 2011; Nicu *et al.* 2013).

The field of retention and drainage is almost unexplored with respect to chitosan. The studies carried out by H. Li and co-workers (Li *et al.* 2004a; Chi *et al.* 2007; Zhang *et al.* 2010) and some preliminary work carried out by Nicu *et al.* (2011) are practically the only references in this area. These studies have demonstrated the potential of chitosan instead of cationic starch as a flocculating agent. In addition, there has been only one study analyzing the possible combination of chitosan with typical microparticles used in microparticles-based retention systems, in this case with anionic silica (Zhang *et al.* 2010). In the cited study, remarkable improvements were observed with the combined use of chitosan and anionic silica. However, there have been no studies regarding the possible

combination of chitosan with other typical components of microparticle retention systems, such as bentonite. Some previous works, which focused on process waters and wastewaters, have demonstrated that bentonite improves the size and density of flocs formed with chitosan, thus increasing flocculation rate (Roussy *et al.* 2005a,b; Cai *et al.* 2010; Miranda *et al.* 2013).

The objective of this work was to analyze the efficiency of three chitosans, differing by molecular weight and charge density, as single retention systems and as part of a microparticle retention systems with bentonite, comparing their efficiency with conventional synthetic polymers such as PEI and PDADMAC. The optimum ratio of polymer to bentonite, flocculation behavior under shear forces, and flocculation mechanisms were analyzed.

EXPERIMENTAL

Materials

Three types of chitosan having different molecular weight and cationic charge density, and two common synthetic cationic polyelectrolytes, PDADMAC and PEI, were tested as retention aids. Chitosan samples, supplied by Sigma-Aldrich Co. (Saint Louis, USA), were Ch.LMW (low molecular weight chitosan), Ch.MMW (medium molecular weight chitosan), and Ch.HMW (high molecular weight chitosan). PDADMAC is a low molecular weight polymer with high charge density supplied by BTG Instruments GmbH (Wessling, Germany), and PEI (Polymin[®] SK) is a medium to high molecular weight polymer with medium charge density supplied by BASF (Ludwigshafen, Germany). The key characteristics of the polymers considered are shown in Table 1.

Table 1. Main Characteristics of Polymers

Polymer	Molecular Weight (kDa)	Cationic Charge Density* (meq/g)	Deacetylation Degree (%)	pH of stock solutions**
Ch.LMW	77	5.4	85.7	4.0
Ch.MMW	293	5.8	86.5	4.0
Ch.HMW	444	3.8	87.5	4.1
PDADMAC	147	6.6	-	6.0
PEI	1600	4.3	-	8.0

* Measured at the pH of the stock solutions.

** The stock solutions were prepared in distilled water for PDADMAC and PEI and in 0.1 M acetic acid for chitosans. The concentration of the stock solutions was 2.5 g/L for PDADMAC, Ch.MMW and Ch.HMW; and 5.0 g/L for PEI and Ch.LMW.

Molecular weight of the chitosan samples was measured by Size Exclusion Chromatography with Multi-Angle Light Scattering (SEC-MALS) according to the procedure described by Tsaih and Chen (1998). Chitosan samples were prepared at 1 g/L concentration in 0.1 M acetic acid and then filtered through 0.45 μ m nylon syringe filter before injection. In this case, two columns PWXL G4000 and G5000 PWXL types (7.8x300 mm, Japan) were connected in series and the mobile phase consisted of buffer 0.2 M acetic acid / 0.1 M sodium acetate pumped at a rate of 0.6 mL/min. The peaks were detected with two on-line detectors: a refractive type detector RI-Optilab REX (Wyatt Technology) and a MALS detector (Multi-Angle Light Scattering) - DAWN HELEOS-II (Wyatt Technology). The calculation of molar mass was carried out according to the Zimm

fit method, using fit degree of 1 and a refractive index increment, dn/dc , of 0.189 mg/mL. The average molecular weight of PDADMAC and PEI, however, were given by the suppliers.

Charge density of the polymers was measured by colloidal titration of the stock solutions with 0.0025 N sodium polyethylene sulphate (PES-Na) using a CAS Charge Analyzing System supplied by AFG Analytic GmbH to measure end point. PEI and PDADMAC were prepared in distilled water, while chitosans were prepared in 0.1 M acetic acid.

The deacetylation degree of chitosans was determined from the FTIR spectrum analysis, using the ratio between the absorbance at the 1320 cm^{-1} and 1420 cm^{-1} peaks as described by Brugnerotto *et al.* (2001). FTIR spectra of chitosan were obtained using the KBr pellet method, using a Thermo Nicolet AVATAR 370 FTIR apparatus. The spectra were determined in the 400 and 4000 cm^{-1} using 128 scans at a resolution of 8 cm^{-1} .

The anionic bentonite used in dual retention systems was Hydrocol OT, a montmorillonite sodium salt type supplied by Ciba (Basel, Switzerland) with a specific surface area of 100 m^2/g and a slight anionic charge (0.235 meq/g). Bentonite was prepared at 10 g/L concentration in distilled water.

The efficiencies of retention aids were tested both in pure ground calcium carbonate (GCC) suspensions and pulp/GCC suspensions. The main interest for papermaking applications is to assess the retention in pulp/GCC suspensions, whereas quantifying the flocculation efficiency in pure GCC suspensions allows a better understanding of the performance of the different retention aids. The GCC suspension was prepared at 0.2% concentration in distilled water. Hydrocarb CL GCC was supplied by OMYA (L'Arbóc, Spain), with the following characteristics: $\text{CaCO}_3 > 98.5\%$; particle mean diameter, 1.8 μm (30% of the particles $< 1 \mu\text{m}$); and surface area, 2.2 m^2/g . The pulp/GCC suspension was prepared from the same GCC and total chlorine free eucalyptus bleached pulp (ENCE, Pontevedra, Spain). This unrefined pulp had a Canadian Standard Freeness (CSF) of 723 mL. The pulp/GCC suspension had 1% consistency (20% GCC related to fibre content). It was prepared by soaking and disintegrating dried pulp in distilled water (2.5% consistency), adding the GCC, and finally, homogenizing and diluting the pulp/GCC suspension to 1% consistency with distilled water.

Methods

Flocculation tests

The measurements were performed using a commercially available focused beam reflectance measurement (FBRM) system (model M500L, Mettler Toledo, Columbia, USA). The FBRM technique measures in real time the chord length distribution of particles in a suspension. 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. Observing the evolution of chord length vs. time it is possible to monitor flocculation, deflocculation, and reflocculation, and the data gathered in the processes can be used to analyze the flocs properties and their flocculation mechanisms (Blanco *et al.* 2002a,b; Ravnjak *et al.* 2006). The measurement duration was set at 5 seconds, which was fast enough to monitor the kinetics of the flocculation, deflocculation, and reflocculation, while maintaining the accuracy of the measurements. Mean chord size (MCS) (μm) and the total number of counts (TNC) (#/s), both for the range 1 μm to 1000 μm , were selected as the main parameters to monitor flocculation (Blanco *et al.* 2002a,b; Ravnjak *et al.* 2006).

Two types of flocculation tests were carried out with single and dual retention systems: flocculation tests and flocculation-deflocculation-reflocculation tests. In flocculation tests, the stirring speed was the same during the process (250 rpm for 0.2% GCC suspension and 400 rpm for 1% pulp/GCC suspension) to maintain the suspension homogeneity while avoiding flocs breakage. In a typical test, after 1 min homogenization and stabilization of the baseline, the polymer was added, and the evolution of the flocculation process was monitored for 5 min. When dual systems were tested, the bentonite was added 5 min after polymer addition, and again the system was allowed to evolve for 5 min. Flocculation tests were used to determine the optimal ratio of polymer:bentonite to be used in dual retention systems and to predict the efficiency of the different treatments in retention and drainage tests.

Flocculation-deflocculation-reflocculation tests were carried out to study the flocs behavior in relation to shear forces. First, the polymer dosage was added after 1 min homogenization of the suspension at low stirring speed (250 rpm for GCC suspension and 400 rpm for pulp/GCC suspension), and the system was allowed to evolve for 4.5 min. Next, bentonite was added, and the system was allowed to evolve for 30 s. The stirring speed was increased to 750 rpm for the GCC suspension and 800 rpm for the pulp/GCC suspension to break the flocs (deflocculation); this speed was maintained for 5 min. Finally, to determine the reflocculation capacity of broken flocs, the stirring speed was reduced to the initial value for another 5 minutes or until the MCS was stabilized. When the polymers were tested alone, deflocculation took place 5 minutes after polymer addition, and reflocculation occurred 5 minutes after deflocculation. All the mixing intensities applied in these studies were selected according to preliminary tests.

From these tests, the strength, or breakage factor (SF), and the reflocculation, or recovery factor (RF), were calculated using Eqs. 1 and 2,

$$SF = \frac{MCS_2}{MCS_1} \quad (1)$$

$$RF = \frac{MCS_3 - MCS_2}{MCS_1 - MCS_2} \quad (2)$$

where MCS_1 is the maximum MCS value before floc breakage, MCS_2 is the MCS value when the flocs were broken after intensive stirring, and MCS_3 is the maximum MCS value for the flocs re-growth after the intensive stirring. All flocculation tests were performed in duplicate.

Retention and drainage tests

First, the effect of increased dosages of polymers (without bentonite) was tested. These treatments were based on the optimal dosages of polymer determined by FBRM measurements in a previous study (Nicu *et al.* 2013). In the present study, the different treatments were tested at half of the optimal dosage (0.5:0), at the optimal dosage (1:0), and at 1.5 times the optimal dosage (1.5:0). Second, the effect of different dosages of bentonite was tested, maintaining the dosage of polymer at the optimal dosage determined by FBRM. The following ratios of polymer:bentonite (by weight) were tested: the optimal ratio obtained in the present study (1:4), a lower ratio (1:2), and a higher ratio (1:6). The first number of these ratios is the dosage of the polymer referred to its optimal dosage determined by FBRM, and the second number is the dosage of the bentonite referred to the

dosage of the polymer used. In addition, four blanks (without any chemical addition) (0:0) were carried out for reference. All treatments are summarized in Table 2.

Table 2. Dosages of Polymers and Bentonite (in brackets) Used in the Tests

Treatment	GCC Suspension (mg/g)					Pulp/GCC Suspension (mg/g)		
	PDADMAC	PEI	Ch. LMW	Ch. MMW	Ch. HMW	PEI / Ch.LMW	PDADM AC	Ch.MMW / Ch. HMW
0.5:0	0.35	1.65	5.4	3.25	2.5	1.05	0.6	0.55
1:0	0.7	3.3	10.8	6.5	5	2.10	1.2	1.1
1.5:0	1.05	4.95	16.2	9.75	7.5	3.15	1.8	1.65
1:2	0.7 (1.4)	3.3 (6.6)	10.8 (21.6)	6.5 (12.5)	5 (10)	2.1 (4.2)	1.2 (2.4)	1.1 (2.2)
1:4	0.7 (2.8)	3.3 (13.2)	10.8 (43.2)	6.5 (26)	5 (20)	2.1 (8.4)	1.2 (4.8)	1.1 (4.4)
1:6	0.7 (4.2)	3.3 (19.8)	10.8 (64.8)	6.5 (39)	5 (30)	2.1 (12.6)	1.2 (7.2)	1.1 (6.6)

Retention and drainage tests were conducted for the pulp/GCC system, using a Müttek-DFR 05 drainage and freeness retention tester (BTG Instruments, Wessling, Germany). In these tests, 1 L of the pulp/GCC suspension at 1% consistency was flocculated at approximately the same shear forces as those used in the flocculation tests monitored by FBRM (1 min homogenization of the sample at 800 rpm, addition of the polymer and mixing during 5 min at 400 rpm, and addition of the bentonite and mixing during 5 min at 400 rpm). The sample was then drained by gravity through a 0.17 mm (150 mesh) metallic wire, and the weight of the filtrate was monitored up to 120 s or a total filtrate weight of 800 g (Fig. 1). Statistics based on the time necessary to achieve a certain weight of filtrate or the weight of filtrate at different times were calculated. The time required to obtain a filtrate weight of 500 g was selected as the most representative statistic to measure drainage time (W500).



Fig. 1. Retention and drainage tests

Additionally, the filtrate was analyzed to measure GCC and total retention. Total retention was calculated from the initial consistency of the pulp/GCC system (1%, 10 g/L)

and the total solids content of the filtrate, measured by drying the filtrate overnight at 105 °C. GCC retention was measured from the initial calcium content coming from GCC in the pulp suspension and the analysis of the calcium content of the filtrate, after acidification with HNO₃ to pH < 2 to dissolve all the suspended calcium carbonate. The calcium measurements were carried out by AAS in a Varian 220 atomic absorption spectrophotometer (Palo Alto, USA). Both retention and drainage tests and the analytical measurements in the filtrate were performed in duplicate.

RESULTS AND DISCUSSION

Determination of the Optimal Ratio Polymer: Bentonite in Dual Systems

To determine the optimal ratio polymer:bentonite, different ratios were tested while maintaining the optimal dosage of each polymer at its optimal dosage (Nicu *et al.* 2013). Five polymer:bentonite ratios (1:2, 1:4, 1:6, 1:8, and 1:10) were tested for GCC suspension and four ratios (1:2, 1:4, 1:6, and 1:8) for pulp/GCC suspension. The presence of bentonite led to an increase of the MCS of the particles to different extents, depending on the polymer used and the considered system. In the GCC suspension (Fig. 2a), the addition of bentonite after PDADMAC and PEI treatments increased the MCS only slightly compared with the single system (1:0), from 13 µm to 18 µm for PDADMAC and from 25 µm to 30 µm for PEI. Higher ratios of polymer:bentonite led to higher increases in the MCS of flocs. The interaction between chitosan and bentonite was much stronger, producing a large MCS increase even at the smallest polymer:bentonite ratio tested (1:2), from 9 µm to 76 µm for Ch.LMW, from 17 µm to 91 µm for Ch.MMW, and from 12 µm to 69 µm for Ch.HMW, as compared with 1:0 treatments. Ch.MMW (the chitosan with the highest charge density and intermediate molecular weight) seemed to interact more strongly with bentonite than Ch.LMW and Ch.HMW, which reflects the importance of electrostatic interactions between chitosan and bentonite.

In the pulp/GCC suspension (Fig. 2b), the observed differences between chitosan and reference products were smaller. Similar improvement of the MCS was obtained for all products, from approximately 12 µm to 16 µm in the case of PDADMAC and from approximately 14 µm to 18 µm to 20 µm for PEI and chitosan. The maximum MCS observed for all polymers occurred at 1:2, while the highest polymer:bentonite ratio (1:8) was the best for PDADMAC.

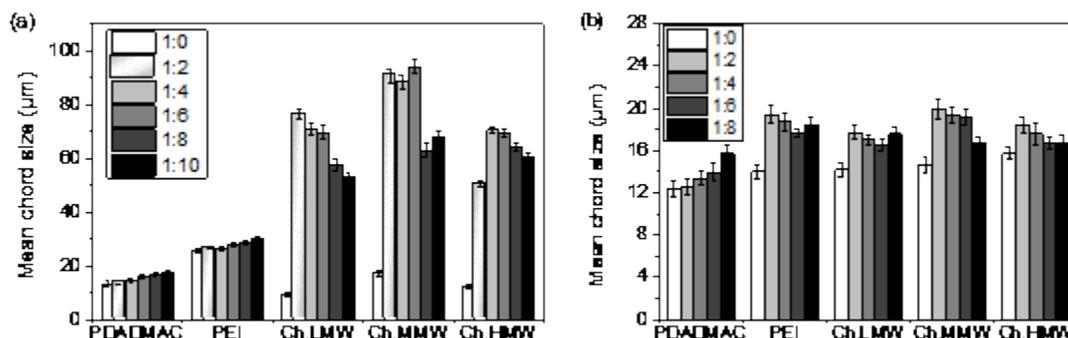


Fig. 2. MCS of the flocs at different polymer:bentonite ratios for (a) GCC and (b) pulp/GCC suspensions

Considering all results, the optimum polymer:bentonite ratio was between 1:2 and 1:4, depending on the polymer and the suspension. In general, a 1:2 ratio is enough for chitosan treatments, but higher polymer:bentonite ratios improved the efficiency of PDADMAC and PEI. Therefore, 1:4 was selected as optimal ratio for the next tests.

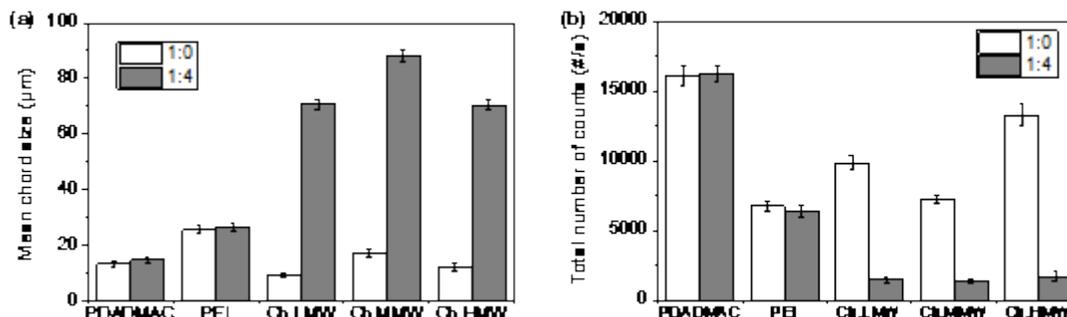


Fig. 3. (a) MCS and (b) TNC obtained with single retention systems (1:0) and dual retention systems (1:4) with GCC suspension

Flocculation Tests: Comparison of Single vs. Dual Treatments

Flocculation at optimal polymer and bentonite dosages

Figure 3a shows the MCS values for GCC suspension after flocculation with single (1:0) and dual systems (1:4). Dual systems always produced an increase of the MCS of the flocs, this being clearly larger for chitosan than for PDADMAC and PEI. The MCS increase for the three chitosans was 60 μm to 70 μm, while it was lower than 2 μm for PDADMAC and PEI. The efficiency of the three chitosans was similar, but Ch.MMW was slightly more efficient than the other two. The final MCS was around 90 μm compared with 75 μm for the other two chitosans.

The strong interaction between chitosan and bentonite was also illustrated by the considerable decrease of the TNC after bentonite addition (Fig. 3b), indicating a large aggregation of GCC particles. While the addition of bentonite did not reduce the TNC with PDADMAC and only a 5% reduction with PEI, chitosan reduced the total number of counts in the suspension by 80% to 90% compared to single systems (1:0).

In the pulp/GCC suspension, the synergy between polymers and bentonite was less obvious, at least in terms of floc size of the flocs (Fig. 4a). After adding bentonite, the MCS only increased slightly: from 12.5 μm to 13.5 μm for PDADMAC, from 14 μm to 19 μm for PEI, from 14 μm to 17 μm for Ch.LMW, from 14.5 μm to 19 μm for Ch.MMW, and from 16 μm to 18 μm for Ch.HMW. Although MCS increases were small, these data must be analyzed together with the TNC evolution (Fig. 4b). After bentonite addition, the TNC increased for all the treatments, contrary to what was expected in flocculation, where there is usually a decrease in the number of particles and an increase in the average particle size. This result indicated there was an important destabilization of dissolved and colloidal material (DCM) that was not previously detected by FBRM probe (1 μm to 1000 μm), as confirmed by the increase in the number of counts in the size range 1 μm to 10 μm (data not shown). As the size of the recently destabilized particles was small compared with the initially present particles and the growing flocs, only a small net increase in the MCS was observed.

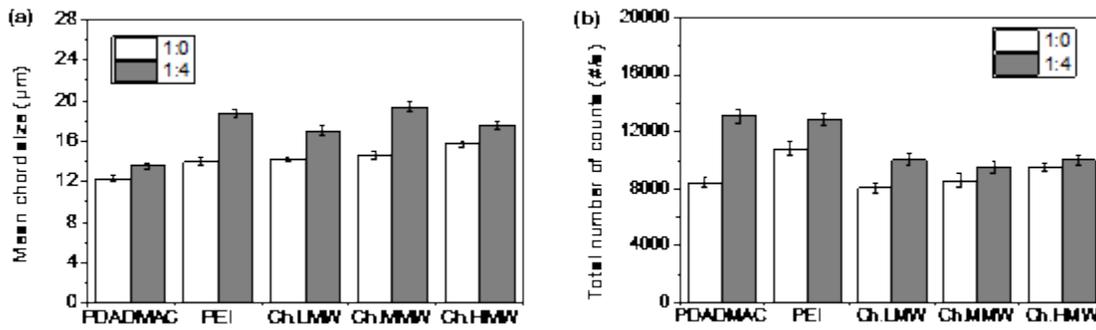


Fig. 4. (a) MCS and (b) TNC obtained with single retention systems (1:0) and dual retention systems (1:4) with pulp/GCC suspension.

Floc behavior under shear forces at optimal polymer and bentonite dosages

Figure 5a and 5b show the flocculation-deflocculation-reflocculation curves for 1:0 and 1:4 treatments. Based on these curves, the strength and reflocculation factors were calculated (Fig. 6).

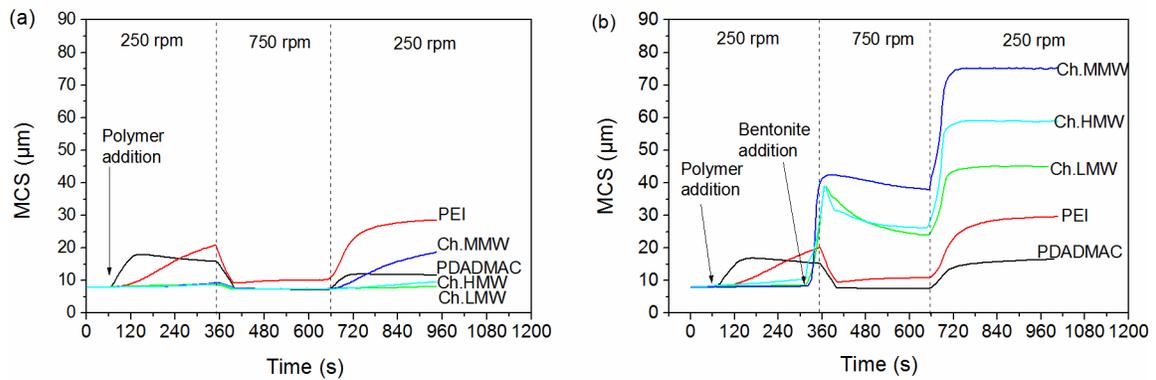


Fig. 5. Flocculation-deflocculation-reflocculation curves in GCC suspension: (a) single retention systems (1:0) and (b) dual retention systems (1:4).

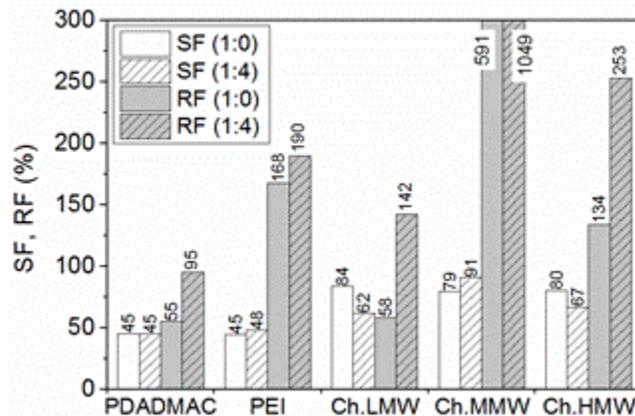


Fig. 6. Strength factor and reflocculation factor for GCC suspension: single vs. dual retention systems.

In the GCC suspension and single system of treatment (1:0), the flocs formed with chitosan were more resistant to shear forces than reference products. The strength factor of the chitosan was approximately 80% to 85% vs. 45% of the reference products when dual systems (1:4) were used. The strength factor did not vary much for the reference products or for chitosan. With chitosan, slight variations in opposite directions were observed; these variations were within the expected experimental error of the measurements.

The reflocculation factor for single systems (1:0) varied largely among the products, following this order: PDADMAC \approx Ch.LMW < Ch.HMW \approx PEI < Ch.MMW. When dual systems were used (1:4), the shear resistance of the flocs almost doubled for all three chitosans and PDADMAC: from 55% to 95% for PDADMAC, from 58% to 142% for Ch.LMW, from 134% to 253% for Ch.HMW, and from 591% to 1049% for Ch.MMW. In contrast, the addition of bentonite only slightly improved the PEI reflocculation factor (from 167% to 190%).

The results obtained with Ch.LMW were very similar to those of PDADMAC, especially in terms of flocs recovery, which agreed with their similar molecular weight and charge density. Ch.LMW had the lowest molecular weight (around 4 to 6 times lower than Ch.MMW and Ch.HMW) and the highest charge density of the chitosans tested (5.4 meq/g). PDADMAC had a slightly higher molecular weight (147 vs. 77 kDa) and the highest charge density of the tested products (6.6 meq/g). High charge density and low molecular weight are the typical conditions for the patch formation flocculation mechanism. The interaction between chitosan and GCC was so strong that the polyelectrolytes adsorbed completely onto the surfaces of GCC despite its relatively low surface potential, as observed previously by Li *et al.* (2004b) with quaternary chitosan. The relatively low strength of the formed flocs and the reflocculation of the broken flocs after shear forces ended are compatible with this flocculation mechanism. After bentonite addition, the strength factor was similar, but the reflocculation ability of the broken flocs increased largely, meaning the main flocculation mechanism was a combination of patch formation and charge neutralization.

Both Ch.HMW and PEI had the highest molecular weight and the lowest cationic charge of the tested products. PEI had a higher molecular weight (1600 kDa vs. 444 kDa) but also slightly higher charge density than Ch.MMW (4.3 meq/g vs. 3.8 meq/g). These characteristics favor a greater contribution from the bridge formation flocculation mechanism. The flocculation of PEI involved a fast aggregation of small particles in the first step, followed by bridge flocculation in a second step, which results in large flocs, as observed previously by Nicu *et al.* (2013). Unlike other high molecular weight polymers, PEI showed not only the capacity to reflocculate the broken flocs under high shear forces but also to form larger flocs than before; while this is in apparent contradiction for bridge formation, it has been observed previously (Nicu *et al.* 2013). The flocculation mechanism of PEI and Ch.HMW seems to be partial charge neutralization with some bridge formation as reflocculation is possible. This behavior could be explained by its branched structure and relatively high cationic charge. The addition of bentonite did not greatly affect the strength factor of the flocs but improved notably the reflocculation factor, especially for Ch.HMW. The small increase of reflocculation factor observed with PEI could be explained by the largest contribution of bridges formation compared to Ch.HMW, which is reasonable according to its considerable higher molecular weight. The interaction of bentonite with the formed flocs is better if the main contribution to flocculation is charge neutralization or patch formation mechanisms (electrostatic interactions). If bridge formation is important, bentonite addition has only a marginal effect.

Finally, the behavior of Ch.MMW was intermediate between partial patch formation and partial bridge formation, as was expected by its intermediate molecular weight and charge density. This product outstands the rest of the products by its high recovery of the broken flocs, which indicated that charge neutralization was the dominant flocculation mechanism in this case.

In the present study, flocculation was a result of charge neutralization, patch flocculation, and polymer bridging, depending on the chitosan molecular weight and charge density, which is in agreement with the main flocculation mechanisms of chitosan when used in coagulation/flocculation processes (Renault *et al.* 2009).

Figure 7 shows the flocculation-deflocculation-reflocculation curves for 1:0 and 1:4 treatments. In the pulp/GCC suspension (Fig. 8), the addition of bentonite (1:4) decreased the strength factor of the formed flocs compared with single systems (1:0) of approximately 15% to 20%, but still had high values. All dual treatments obtained similar results in terms of strength varying from 72% to 85%.

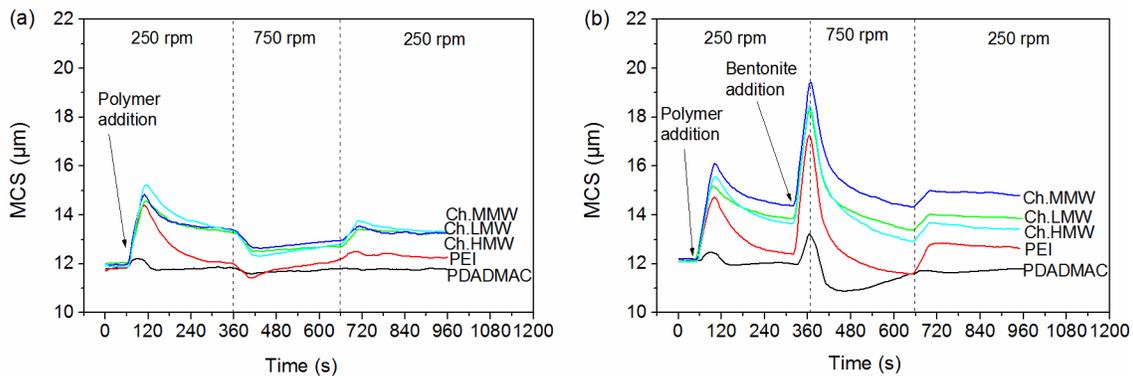


Fig. 7. Flocculation-deflocculation-reflocculation curves in pulp/GCC suspension: (a) single retention systems (1:0) and (b) dual retention systems (1:4)

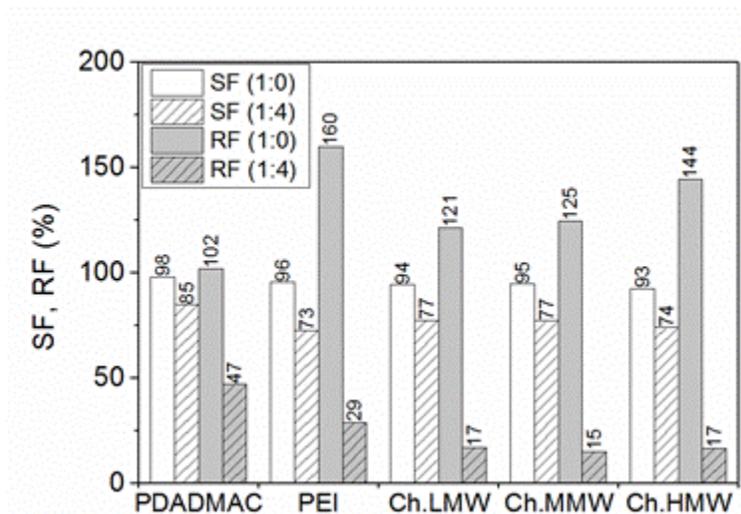


Fig. 8. Strength factor and reflocculation factor for pulp/GCC suspension: single vs. dual retention systems

The reflocculation process was not improved in any case by bentonite addition, even for chitosan. The flocs no longer recovered at the same level as they were initially. In single systems, the reflocculation factor varied from 100% (PDADMAC) to 160% (PEI), with chitosan at intermediate values of 120% to 150%. After bentonite addition, the reflocculation factor decreased to 30% for PEI and 50% for PDADMAC, and 15% to 20% for the three chitosans. The largest decrease in reflocculation behavior for the highest molecular weight polymers could be due to a partial shift to bridge formation as confirmed by the larger flocs in dual compared with single systems, especially for chitosan. In dual systems, bentonite could act as a bridging agent between the cationic sites created by the cationic polymer when added to the pulp pretreated by chitosan. Similar behavior was observed in a previous study carried out by Zhang *et al.* (2010), where quaternary chitosan was used in combination with anionic silica for the treatment of reed pulp. In the cited study, the quaternary chitosan formed flocs of low resistance, suggesting that patch formation was the predominant flocculation mechanism. However, in dual systems, the system evolved to bridge formation. Consequently, the strength of the flocs increased, and the reflocculation of the broken flocs was possible. This bridge formation mechanism has been also recognized by Renault *et al.* (2009) when cationic chitosan derivatives were used to flocculate anionic inorganic bentonite suspensions. The evolution to partial bridge formation should increase the strength factors of the flocs formed in dual systems compared with single systems, but this effect was not observed in the present study.

Retention and Drainage

Single systems

As shown in Fig. 9a, the total retention increased in all cases with increasing polymer dose. Because unrefined pulp was used, the total retention of the blank test (without using any retention aid) was as high as 86.8%.

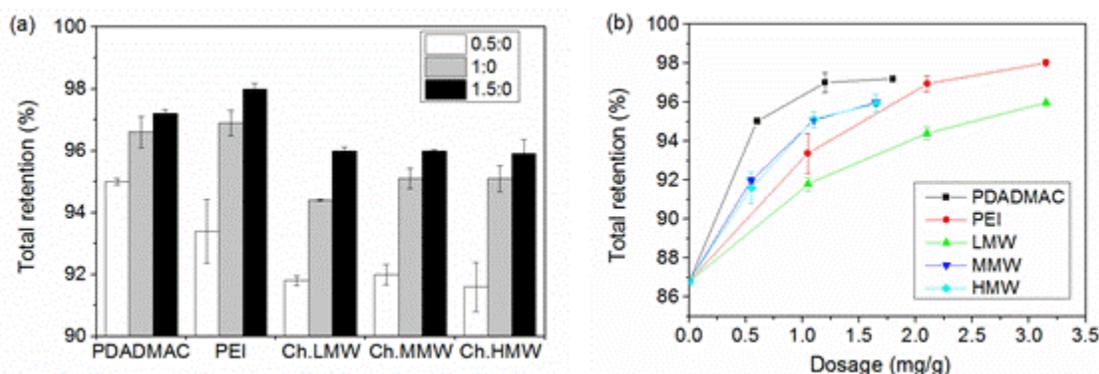


Fig. 9. Total retention with single systems at: (a) optimal dosages determined by FBRM, and (b) dosages in mg/g pulp/GCC suspension.

At the optimal dosage of each product, the total retention was higher with conventional polymers than with chitosan. At the optimal dosage (1:0), PEI and PDADMAC resulted in similar values for total retention (approximately 97%), while the three chitosans yielded values approximately 94% to 95% with minor differences among them. Notably, the optimal dosages of polymers were different (1.1 mg/g to 2.1 mg/g; Table 2). If total retention is represented vs. the dosage of polymer (expressed as mg/g

suspension), it can be seen that Ch.MMW and Ch.HMW led to higher total retention values than PEI at the same dosage, but still lower than those of PDADMAC (Fig. 9b).

For all polymers, the difference between the total retention at lowest dosage (0.5:0) and the optimal dose (1:0) was substantial; the total retention increasing by 2.6% to 3.5%, except for PDADMAC (1.6%). The difference between the total retention at optimal dose (1:0) and at 50% higher dosage (1.5:0) was much lower, varying between 0.6% and 1.6%, confirming the validity of the optimal dosages determined by FBRM.

Figure 10a shows the GCC retention for single systems. GCC retention for the blank was 28.1% due to filtering of the pulp. A similar 20% CaCO₃ retention was obtained in the study of Chi *et al.* (2007) when retention aids were not used.

GCC retention followed a similar trend to total retention. The conventional polymers were more efficient than the three chitosans at optimum dosage. GCC retention ranged from 85% for PDADMAC to 87% for PEI, while it varied from 71% for Ch.LMW and 75.5% for Ch.LMW to 77% for Ch.MMW for the chitosans. The difference between conventional polymers and the most efficient chitosan was still important, about 10%. At 1.5:0 dosage, Ch.MMW obtained GCC retention values similar to that of conventional polymers (84%), which is important taking into account that the optimum dosage used for Ch.MMW was half that of PEI. The GCC retention values obtained in the present study were higher than in previous studies; for example, a maximum of 80% GCC retention was obtained with quaternized chitosan for the flocculation of peroxide bleached reed kraft pulp with 20% GCC (Chi *et al.* 2007).

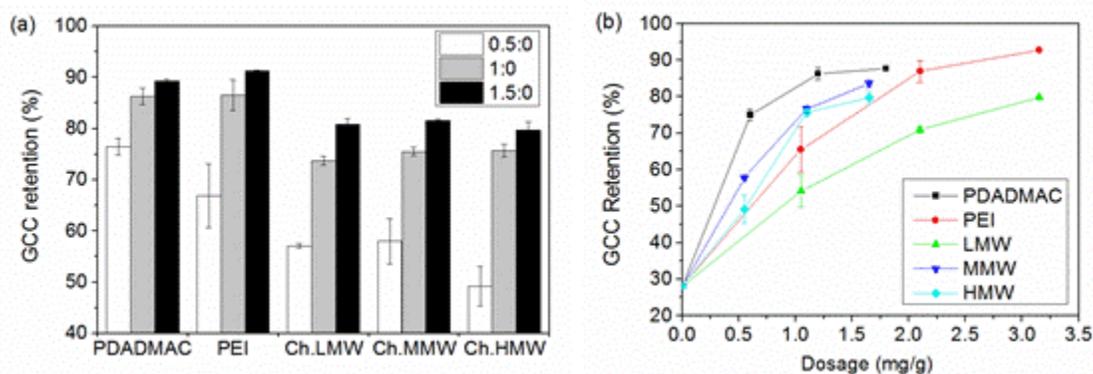


Fig. 10. GCC retention with single systems at: (a) optimal dosages determined by FBRM, and (b) dosages in mg/g pulp/GCC suspension

As with total retention, at intermediate doses of around 1 mg/g, PDADMAC was again the most effective polymer, and the two most effective chitosans (Ch.MMW and Ch.HMW) were more efficient than PEI (Fig. 10b). These results demonstrated that molecular weight has a greater impact than charge density in achieving a better retention, with higher molecular weights being beneficial for obtaining higher retention values. These results seem to contradict the study of Chi *et al.* (2007). In the cited study, the required optimal dosages were higher at higher molecular weights, *i.e.*, lower molecular weights were more efficient for higher retention of CaCO₃. However, due to the low molecular weight of the chitosan tested (from 48 kDa to 190 kDa), electrostatic interactions were the only interactions present, and it is well known that these electrostatic interactions (patch formation/charge neutralization) are enhanced at lower polymer molecular weights. Again,

the optimal dosage determined by FBRM adequately predicted the efficiency of these polymers in GCC retention.

Figure 11 shows the values obtained for W500 (the time required to drain 500 g of the filtrate) for the different single treatments. The drainage time for the blank was around 12 s. The most efficient polymer in terms of drainage rate was Ch.MMW (average 10 seconds), followed by Ch.LMW (average 11.5 seconds). The other three polymers obtained lower drainage rates, around 12 seconds for PEI, 13 seconds for Ch.HMW, and 14 seconds for PDADMAC. Thus, in single systems, Ch.MMW and Ch.LMW were the only products that reduced the drainage time compared with the blank. In contrast, PDADMAC and PEI lead to a lower drainage rate. This could be due to the floc structure. More open floc structure corresponds to larger and less compact flocs, which produced a faster drainage in the initial stages. Furthermore, conventional polymers retained more mineral fillers, which can cover the gaps of the cake and reduce the drainage rate.

In terms of drainage, there is an important benefit when chitosan is used. In the study carried out by Chi *et al.* (2007), for example, the drainage rate obtained with quaternized chitosans was 20% faster than cationic starch. In the present study, a similar 20% average decrease was obtained with Ch.MMW compared with conventional treatments based on PDADMAC and PEI. This important issue reflects that drainage is a major factor in industrial operation as it is related to the paper machine speed (and thus, the productivity) and the energy consumption (Zhang *et al.* 2010).

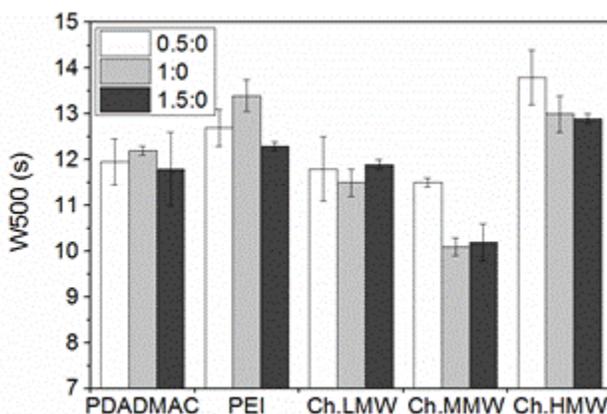


Fig. 11. Drainage time with single retention systems

Dual systems

Figure 12 shows the effect of bentonite on total retention. For PDADMAC and PEI, the addition of bentonite did not increase noticeably the degree of flocculation. For PEI, the results are even worse than in single systems, as partial bridge flocculation impaired the electrostatic interaction with anionic bentonite. For chitosan, an important synergy with the bentonite was observed. The greatest synergy was observed with Ch.LMW; total retention increased by 2.5%. Although total retention obtained by Ch.LMW was the lowest in single systems (94.4%), the total retention in dual systems was the highest of the chitosans (96.9%), which was very close to that obtained by the reference products. With the other two chitosans, the synergy with bentonite was less important. Total retention increased from 95.1% to 96.4% with Ch.MMW and from 95.1% to 96.1% with Ch.HMW (1:2 or 1:4 in both cases). Again, this is explained by the importance of electrostatic interactions when anionic bentonite is used.

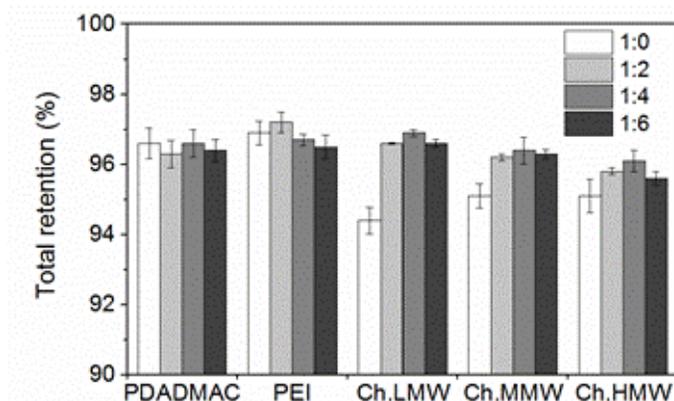


Fig. 12. Total retention with dual retention systems

As predicted by preliminary results, both 1:2 and 1:4 could be the optimum ratio polymer:bentonite in terms of total retention. Although bentonite was used in a ratio 1:2 or 1:4 compared with the chitosan dosage, its price is considerably lower than the cost of PEI, PDADMAC, and even much more in the case of chitosan and will not affect much the cost efficiency of the whole treatment.

The addition of bentonite also improved GCC retention, especially for chitosan (Fig. 13). Despite the great synergy of chitosan and bentonite, synthetic polymers were still slightly more efficient in GCC retention. With PDADMAC, the GCC retention increased from 85% at 1:0 to 90% at 1:6, and with PEI, from 87% at 1:0 to 90% at 1:4 dose. Again, the synergy with bentonite was especially important with the low molecular weight and high charge density chitosan (Ch.LMW). In this case, GCC retention increased from 71% at 1:0 to 86.5% at 1:4, which was similar to the results of the synthetic polymers in single systems and only slightly less efficient (3%) than those obtained in dual systems. However, these differences would be easier to overcome in real process conditions, especially taking into account the large differences in drainage rate. Although bentonite addition increased the efficiency of the other two chitosans, this increase was lower than for Ch.LMW: from 77% to 83.5% for Ch.MMW and from 76% to 79.5% for Ch.HMW (1:4 values compared to 1:0 values). As observed in total retention, the optimum polymer:bentonite ratio was 1:2, as only small improvements were obtained at higher ratios.

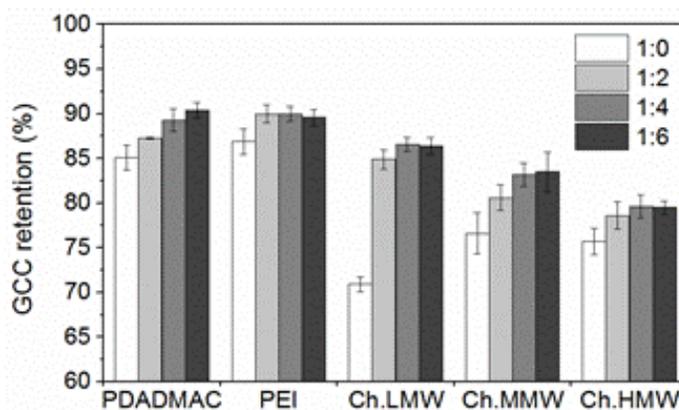


Fig. 13. GCC retention with dual retention systems

Notably, the dosage of Ch.LMW was the same as PEI (2.1 mg/g) but was around double the amount of the other chitosans and PDADMAC. Thus, the optimum dual treatment in an industrial application would be based on Ch.MMW instead of Ch.LMW.

Although chitosan had a faster drainage than reference products when single systems were used, the presence of bentonite (Fig. 14) enhanced this trend. The value of W500 decreased for all polymers compared with single systems; however, among all the polymers, Ch.MMW and Ch.LMW were again the two most effective. The drainage time of these chitosans was 20% to 35% lower than PEI and 35% to 45% lower than PDADMAC. At the 1:4 dosage, Ch.MMW and Ch.LMW obtained a drainage time of 8.0 s and 7.9 s, respectively, compared with around 12.5 s for PEI and 12 s for PDADMAC.

According to the results obtained, the dual system with Ch.LMW was the best option both for retention and drainage. However, as commented before, Ch.MMW presented similar efficiency in retention and drainage at around half the dosage (1.1 mg/g vs. 2.1 mg/g). Importantly, if chitosan was used in simple systems, the most effective was Ch.MMW or Ch.HMW, while Ch.LMW was the most efficient in dual systems, followed by Ch.MMW.

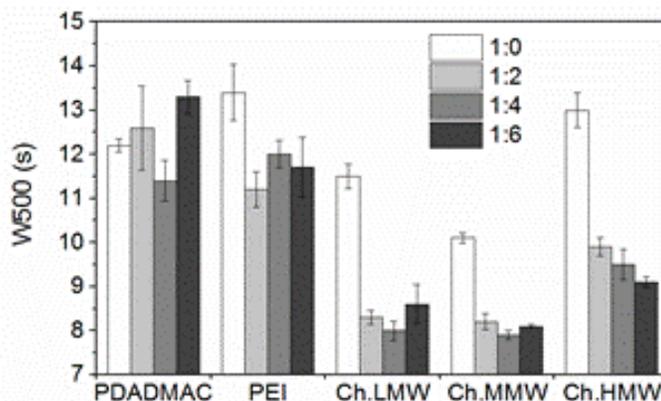


Fig. 14. Drainage time with dual retention systems

Results demonstrated that dual treatments based on chitosans and bentonites can obtain similar retention values as those achieved with conventional synthetic polymers but faster drainage rates. These results were obtained by native chitosans despite the fact that pH values of the pulp/GCC and GCC suspensions were alkaline: pH 8.8 for pulp/GCC suspension and pH 9.5 for GCC suspension. This is an apparent contradiction with the fact that native chitosans lose their charge and precipitate from solution at neutral and alkaline pH values. Native chitosans are usually modified if they are to be used at alkaline conditions. For example, in the work of Li *et al.* (2004a), also testing the possibility of chitosans to be used as retention aids in alkaline papermaking, quaternary chitosans were used.

In a previous work carried out by the authors, the effect of pH on chitosans charge was determined. The charge density of the chitosans was almost constant at acidic pH while decreasing sharply at pH > 6, losing their charge and precipitating at around pH 7.5 (Miranda *et al.*, 2013). However, the GCC and pulp/GCC suspensions flocculate well at pH around 9. This apparent contradiction can be explained by the acetic acid used for their preparation, which produced a pH shock in the suspension after chitosans addition. After pH shock, the pH increases slowly back to a slightly lower value than the initial pH of the suspension, *i.e.* pH 8.3-8.4 for pulp/GCC suspensions. However, due to the fast kinetics of

agglomeration, flocculation was complete within a few seconds (Nicu *et al.* 2013) and occurred at acidic pH, *i.e.* pH from 4.5 to 6.0, well below the pH solubility limit of chitosans, *i.e.* from pH 4.5 to 6. When the pH returns back to the initial value, the pH solubility limit is exceeded, and the chitosans will become insoluble. However, the flocs formed at acidic conditions were not impaired at all by this fact. This is something similar to what Myllytie *et al.* (2009) observed. In the cited study, the adsorbed chitosan layer remained on the cellulose surface even when the pH was increased to pH 8-10 (solubility limit of the chitosan used in that study was pH 6.8). Furthermore, the wet adhesion between chitosan-coated cellulose surfaces and thus the wet strength of paper was improved at pH higher than the solubility limit of the chitosan (pH 7-8).

Extrapolation from laboratory conditions to full scale is potentially hazardous and must be done carefully with additional research, although, in a previous study in which two of the chitosans used in this work were used to remove contaminants in a dissolved air flotation, with industrial process waters from newsprint production, they obtained higher efficiency than their quaternary modifications and the initial pH of waters was 7.7 (Miranda *et al.* 2013).

As observed, the combination of bentonites with chitosans improved retention greatly, which was the main drawback of chitosans in single systems, while still slightly increasing the drainage rate. Bentonites act by electrostatic forces, bringing together the microflocs previously formed by the chitosan, creating a porous, tight floc structure which usually deforms, losing its strength and enabling high retentions and good sheet formation (Mohit and Seshachala 2011).

Clearly, other dual components based on a bridging effect may be used with chitosans to achieve similar results. In this sense, anionic polyacrylamides (A-PAM) could be an alternative to the use of bentonites. However, given that one of the main aims of the study was to substitute synthetic (conventional) polymers by eco-friendly alternatives, it was decided not to test chitosans with A-PAM, even though the combination could also be efficient. In fact, some recent studies have focused on developing hybrid coagulants for improved flocculation properties, grafting polyacrylamide onto chitosans, which also improves the solubility of chitosans at alkaline pHs (Ali and Singh 2009; Lu *et al.* 2011; Wang *et al.* 2015). Nevertheless, further research would be needed as bentonites has unique characteristics helping for the retention of colloidal and complex dissolved solids as well as fiber, fines, and minerals (Mohit and Seshachala 2011).

CONCLUSIONS

1. Chitosan was always more efficient for drainage but somewhat less effective for GCC retention than PDADMAC and PEI. In single systems, the drainage time observed with chitosans was on average 20% faster than with PDADMAC or PEI. Total retention with PDADMAC and PEI was similar to that obtained by chitosans (96-97% *vs.* 94-95%); however, the GCC retention was much higher (85-87% *vs.* 77% for Ch.MMW) (1:0 dosage). This situation was greatly improved by using dual systems with bentonite (1:2 or 1:4 ratios). The greatest synergy occurred with the lowest molecular weight and high charge chitosan (Ch.LMW), which obtained similar total and GCC retention than synthetic polymers (95% total retention, 87% GCC retention) and 30% faster drainage rate than PDADMAC and PEI.

2. Flocculation with chitosan was interpreted as a result of charge neutralization, patch flocculation, and/or polymer bridging, depending on the molecular weight and charge density of the chitosan. The greatest synergy of chitosan and bentonite was observed when the main flocculation mechanism was based on electrostatic interactions, while it was minimum when the partial bridge mechanism was taking place.
3. Native chitosans were efficient in flocculating GCC and pulp/GCC suspensions at alkaline pH due to the pH shock produced by the acetic acid used in their preparation which allows a fast flocculation occurring at acidic pH, which was not impaired even when the pH back around the initial values and the chitosan became insoluble.
4. Although chitosan is more expensive than conventional polymers, the faster drainage rates and the expected lower energy consumption in paper machine could compensate its cost, especially if native instead of quaternized chitosans can be used at alkaline pH at industrial scale. Furthermore, additional tests regarding the mechanical properties of the paper handsheets should be considered together with the retention and drainage results. Nevertheless, chitosan is a promising eco-friendly alternative to conventional polymers as retention aids, especially if used in dual systems with bentonite microparticles.

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