CELLULOSE CHEMISTRY AND TECHNOLOGY

CHITOSAN AS CATIONIC POLYELECTROLYTE IN WET-END PAPERMAKING SYSTEMS

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Received October 1, 2010

This paper provides the experimental results evidencing the potential of chitosan utilisation as a wet-end additive in papermaking. The research analyzes the colloidal behaviour of chitosan, investigated in terms of its interactions with the anionic polymers (carboxymethylcellulose – CMC, and anionic polyacrylamide – PAA), as well as with the colloidal and dissolved material (CDM) of papermaking process water. The shape of colloidal titration curves and particle size distribution of process water, measured by laser diffraction, have indicated that chitosan has a higher ability to form polyelectrolyte complexes (PEC), comparatively with other cationic additives frequently used in wet-end systems, such as PDADMAC and polyethylenimine (PEI). Lab tests simulating short circuit of paper machine have shown that chitosan and PDADMAC have similar effectiveness in reducing the accumulation rate of CDM, even if the effects on paper stock drainage and paper strength are much higher in the case of chitosan.

Keywords: chitosan, colloidal and dissolved material (CDM), polyelectrolyte complexes, colloidal titration, coagulant, process water

INTRODUCTION

General background

Papermakers use various chemical additives to enhance the product's end-use performance, as well as the efficiency of the manufacturing process. Chemicals also have an important contribution to reducing the environmental impact and, if one were to omit all chemical additives from a papermaking process, the consequences would include larger increases in emissions. However, in view of the currently more authoritative measures of environmental concern and the prediction[1] for a significant increase of chemical usage (from 3.6 million tons in 2000 to above 6 million tons in 2020), papermakers and suppliers have to seriously consider the potential environmental impact of the chemical additives. In this context, part of our challenge in maximizing the efficiency of papermaking operations and making them increasingly eco-friendly is to envision new types of additives, such as bio-chemicals.[2]

Papermaking bio-chemicals could be defined as compounds obtained from renewable resources, biodegradable and applicable for process or paper quality improvement. These types of compounds are based on organic macromolecules of biological origin (bio-polymers) represented mainly by polysaccharides, such as starch, cellulose derivatives and chitosan.

Chitosan characteristics

Cationic biopolymer

Chitosan is the main derivative of chitin, which is the second polysaccharide on earth, after cellulose. The terms chitin and chitosan refer to a heteropolymer chain with $\beta(1\rightarrow4)$ linked D-glucosamine or N-acetyl-D-glucosamine residues with different substitution patterns.[3,4] The unique structural feature of chitosan is the presence of primary amines at the C-2 position of the D-glucosamine residues. These amine groups first allow specific chemical reactions, and second, they confer important functional properties to chitosan, which can be exploited for numerous applications.

In a solid state, chitosan molecules organise themselves into ordered crystalline regions co-existing in an amorphous phase, being considered as a semi-crystalline polymer.[5,6] The degree of crystallinity and the molecular structure are key factors, underlying solubility, mechanical strength and other functional properties of chitosan. In contrast to chitin, the presence of free amine groups along the chitosan chain allows this macromolecule to dissolve in dilute aqueous acidic solvents. In a dilute acidic medium, the following equilibrium occurs:[3,7] $-NH_2 + H_2O^+ \Leftrightarrow -NH_3^+ + H_2O$. The emergence of positive charges on the chains explains the polyelectrolyte character of chitosan and influences its properties.[8,9] The charged state and properties of chitosan are substantially altered by the pH level. At a low pH (< 6), the amine groups are protonated and positively charged, conferring a polycationic behaviour to chitosan. At a high pH (above 6.5), the amine groups of chitosan are deprotonated, the polymer loses its charge and becomes insoluble. Chitosan's pK_a is close to neutrality,[8,10,11] and the soluble–insoluble transition occurs at pH values between 6 and 6.5, which could be a particularly well-situated range for papermaking applications. Also, at a pH above 6.5, the electrostatic repulsions of chitosan are reduced, permitting the formation of inter-polymer associations, which can lead to fibres, films, networks, hydrogels, depending on the conditions used to initiate the soluble–insoluble transition.[12]

Film forming, biodegrability, antimicrobial activity

Unquestionably, one of the most interesting properties of chitosan is its film-forming ability. As chitosan can be dissolved under slightly acidic aqueous conditions, it can be readily cast into membranes or films with good mechanical and permeability properties.[3,13,14] Enzymatically, chitosan can be easily depolymerised by a variety of hydrolases. Beyond complete biodegradability, other characteristics are present in chitosan, such as low toxicity and excellent biocompatibility.[7,14] Chitosan has exhibited a high antimicrobial activity against a wide variety of pathogenic and spoilage microorganisms, including fungi, and Gram-positive and Gram-negative bacteria.[15]

Chitosan applications

Due to its biodegradability, biocompatibility, antimicrobial activity, non-toxicity and versatile chemical and physical properties, chitosan has a great potential for a wide range of applications. The present tendency is toward high-value products, like cosmetics, food additives, drug carriers, pharmaceutics and semi-permeable membranes.[4,7,16] However, early applications of chitosan concerned its use as a chelating and coagulating agent for wastewater treatments.[7,17] At present, there are few applications of chitosan in papermaking, related mainly to surface treatments of specialty papers, such as photographic and carbonless copy paper.[18] However, more and more numerous researchers are investigating the potential applications of chitosan as a papermaking additive, for both internal and surface applications. Several studies focus on the use of chitosan for improving the wet and dry strength of paper,[19-22] others demonstrate the compatibility of chitosan with paper stock components and its ability to work as a retention and drainage additive,[23] or as dye fixative in producing coloured paper.[24] The inherent antibacterial properties and the film-forming ability of chitosan are also studied for potential applications in papermaking and paper finishing.[25,26]

Objectives

The objectives of the here reported investigation were to study the colloidal behaviour of chitosan under wet-end papermaking conditions, observing the interaction of chitosan with anionic compounds and the effectiveness of chitosan as a coagulant.

EXPERIMENTAL

Experimental approach

Interaction of chitosan with anionic compounds. Firstly, the interaction of chitosan (CH) with the carboxymethylcellulose (CMC) and anionic polyacrylamide (PAA) was analyzed by colloidal titration, comparatively with other two cationic polymers, respectively, poly-diallyl-dimethyl-ammonium-chloride (PDADMAC) and polyethylenimine (PEI). Secondly, the interaction of chitosan with the colloidal and dissolved material (CDM) from the process water of a papermaking system, based on OCC-recovered paper as fibre raw material, was investigated by the colloidal titration and particle size distribution for different grades of anionic charge neutralization. The tests were performed with the same cationic chemicals of the first step.

Effectiveness of chitosan as a coagulant in wet-end papermaking system. The effectiveness of chitosan as a coagulation agent was evaluated by a lab simulation of a paper machine short circuit on the DDJ (Fig. 1), comparatively with PDADMAC. The coagulant dosage was calculated for each cycle, to neutralize 70% of anionic charge of each sample (based on the cationic charge demand – CCD – of the stock, and on the charge density – CD –of cationic polymers). The sample of process water after 10 cycles (A - without coagulant) was used in the first two steps of the study (colloidal titration and particle size distribution) and to dilute the stock for handsheet forming.

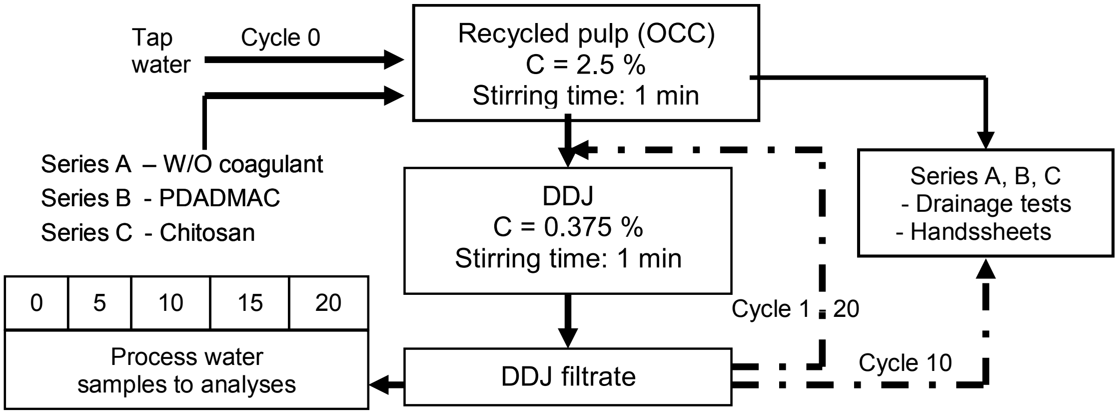


Figure 1: Experimental concept to evaluate coagulants as wet-end additives

Materials

Fibre raw material: recovered paper of old corrugated containers (OCC).

Chemicals: standard polymers for colloidal titration (PDADMAC and PESNa, 0.001 N solutions); PDADMAC – low molecular weight (MW), cationic charge density – CD = 2.6 meq/g (Ciba Speciality Chemicals product); chitosan – medium MW, acetylating degree – 20.3%, cationic CD = 3.7 meq/g (Vanson, Inc product); PEI – high MW, CD = 4.05 meq/g (BASF product); CMC – SD = 0.9, anionic CD = 2.5 meq/g (Kalle Nalo GmbH product); PAA – high MW, anionic CD = 1.70 meq/g (Ciba - Percol 155).

Analysis methods

Colloidal titration was manually performed on a Mütek PCD-02 apparatus to obtain colloidal titration curves, and to measure the CD of the polymers and CCD of the paper stock and process water.

Particle size distribution of the papermaking process water, before and after the treatment with coagulant chemicals, was obtained on a SHIMADZU Laser Diffraction Particle Size Analyzer.

Process water analyses were performed following a methodology developed in our laboratory,[27] which involves two categories of analyses: *preliminary analyses* – pH, ionic charge density and turbidity; and *quantitative analyses* – CDM and its composition (starch, lignin, extractives and polysaccharides). All analyses are related to the supernatant fraction that was obtained by centrifugation of process water samples collected after 0, 5, 10, 15, 20 cycles (Fig. 1).

Effects of chitosan and PDADMAC on papermaking processes and paper properties were evaluated by: drainage time (DT) – time needed for collecting 700 mL filtrate by drainage of 1 L stock suspension (c = 3 g/L) on a Shöpper Riegler apparatus; total first pass retention and CDM retention were calculated considering the results of the filtrate analyses (from cycle 10) on a DDJ apparatus; paper handsheets were obtained on a lab former (grammage = 70 g/m^2) and were characterized by standard methods as to breaking length and water absorption capacity – Cobb$_{60}$.

RESULTS AND DISCUSSION

Interaction of chitosan with anionic compounds

CMC and anionic PAA have been chosen for colloidal titration tests in view of the fact that both chemicals may occur as components of different additive systems, due to their similarities (anionic charge, slightly alkaline pH of diluted solutions), and to their different chemical structure and molecular weight. The shape of the colloidal titration curves (Figs. 2 and 3) shows clear deviations from 1:1 stoichiometry of the interaction between oppositely charged polymers. The curves present similar trends for both anionic polymers, but significant differences among cationic polymers.

PDADMAC, a standard titration polymer, is assumed to be the most resistant to stoichiometric interaction. Considering that the shapes of the titration curves could indicate the strength of complexation between the two polyelectrolytes,[28,29] one can suppose that chitosan has a higher ability to form polyelectrolyte complexes (PEC), comparatively with PDAAMAC and PEI. Therefore, the formation of electrostatic PEC between chitosan and synthetic or natural polymers is frequently cited in the literature.[7,30]

The titration curves of CDM from process water with the three cationic polymers present significant changes compared to those of individual anionic polymers (Fig. 4). It could be observed that in the case of PDADMAC and chitosan, the streaming potential output began to change right from the start of the titration. An opposite change could be remarked for PEI, which showed a slower neutralization rate and an extension of curve flatness. These results were confirmed by FTIR spectra analysis of the separated precipitate, which evidenced characteristic absorption bands of chitosan (1621 cm^{-1}, 1380 cm^{-1}) as well as by the analysis of particle size distribution in process water. The results evidenced clearly a different colloidal behaviour of the three cationic polymers: at 100% charge neutralization, PEI did not induce the coagulation of CDM, the particle size distribution curve being overlapped with that of the blank sample (Fig. 5); PDADMAC produced a fast coagulation at the neutralization degree of around 50% and chitosan at a degree higher than 60% (Table 1). Compared to PDADMAC, chitosan showed a higher potential for electrostatic complexation, which resulted in larger particles of CDM precipitate.

Effectiveness of chitosan as coagulant in wet-end papermaking system

The simulation of process water recycling in the short circuit of a paper machine was performed without additives and with PDADMAC and chitosan at dosages for a 70% neutralization degree of the anionic charge. A summary on the effects of the two additives on the characteristics of the process water is presented in Figures 6-9. In the absence of coagulants, the accumulation rate of the colloidal and dissolved materials is very high in the first 10 cycles, a stabilization trend, even a slight decrease, being visible in the following cycles (Figs. 6 and 7). The shape of the curve is similar when the coagulants were applied, but the concentration levels are consistently lower. The main component of CDM consists of the polysaccharides and all components show about the same accumulation rate in the absence of the coagulants (Fig. 7). The accumulation rate of the polysaccharides decreases by about 55% for PDADMAC and by 50% for chitosan (Fig. 8), but the accumulation rate of the other disturbing substances of the wet-end chemistry are reduced more consistently (Fig. 9). After 10 recycling cycles, when the maximum CDM accumulation is reached, the application of chitosan produces reductions of about 80% of the starch and of about 90% of the extractives contents in the process water.

The effects of the two coagulants on the processes and paper characteristics are presented in Table 2. The paper stock for these tests was prepared from recycled pulp with the addition of AKD emulsion as a sizing agent (0.1% o.d. reported to fibre dry matter), without and with the addition of coagulants (series B – 0.65% PDADMAC, series C – 0.45% chitosan).

Table 1
Average particle size in process water as a function of
charge neutralization degree with different cationic polymers

Charge neutralisation, %	Average particle size, µm		
	PDADMAC	Chitosan	PEI
0	0.029	0.029	0.029
25	0.028	0.028	0.028
50	0.463	0.028	0.029
75	0.466	0.893	0.029
100	0.891	7.319	0.029

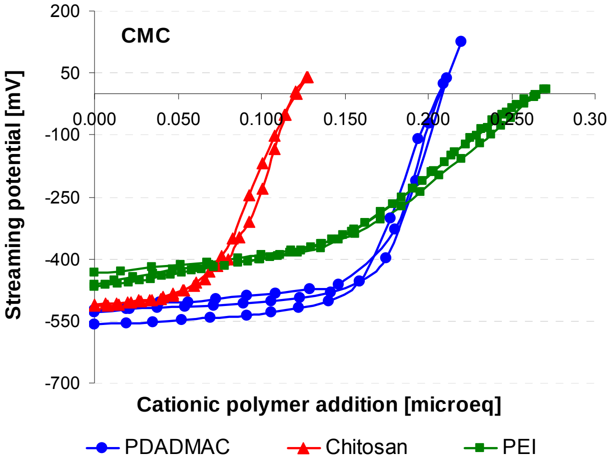


Figure 2: Colloidal titration curves of CMC solution (0.1 g/l) with cationic polymers

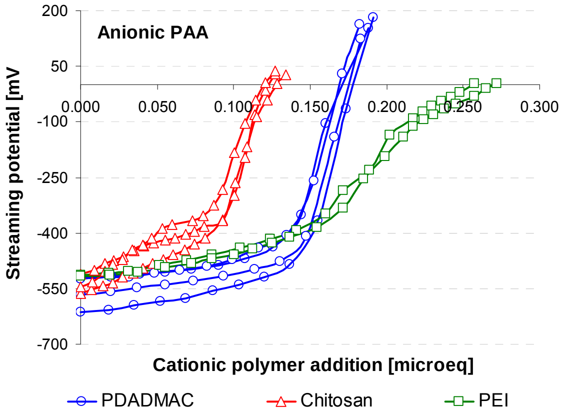


Figure 3: Colloidal titration curves of anionic PAA solution (0.1 g/l) with cationic polymers

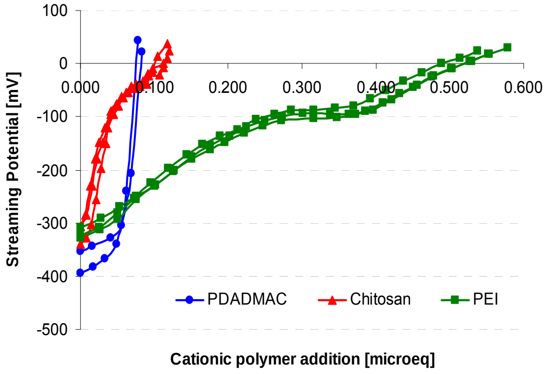


Figure 4: Colloidal titration curves of process water with different cationic polymers

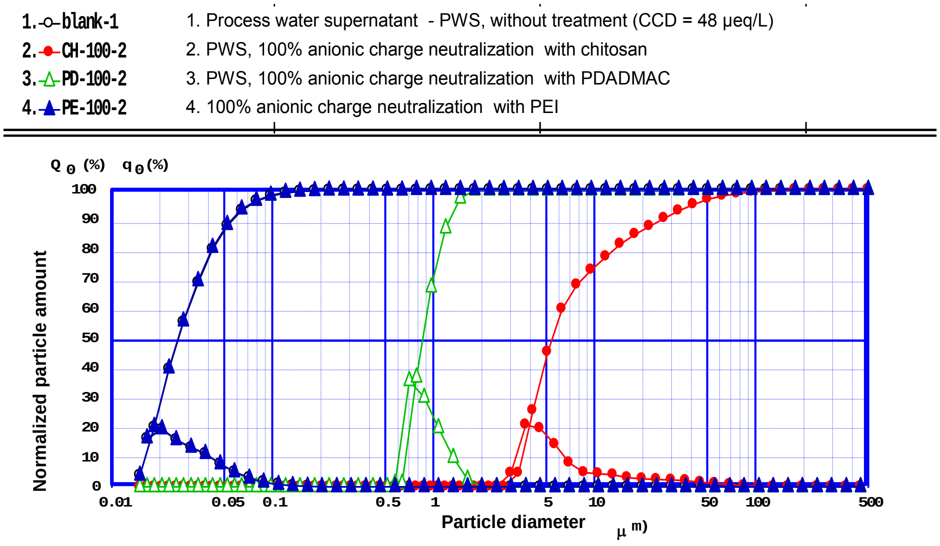


Figure 5: Particle size distribution in process water before and after treatment with cationic polymers for total neutralization of anionic charge

Table 2
Effects of coagulants on papermaking processes and paper properties

Experiment series	Turbidity, BSU	Drainage time, s	Retention of CDM, %	Breaking length, m	Cobb$_{60}$, g/m^2
A. Without coagulants	395	75	reference	2950	65
B. PDADMAC, 0.65%	58	35	53.3	3700	36
C. Chitosan, 0.45%	38	22	51.2	3050	23

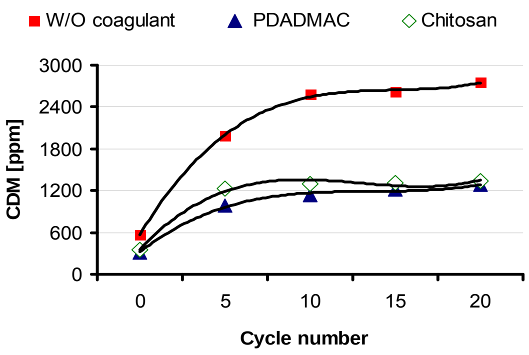


Figure 6: Effect of coagulants on CDM accumulation by process water recycling

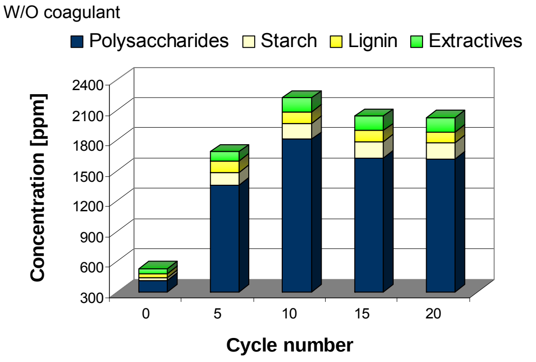


Figure 7: Composition of CDM as a function of water recycling cycles

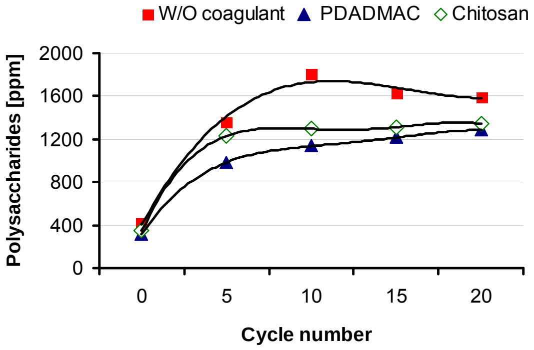
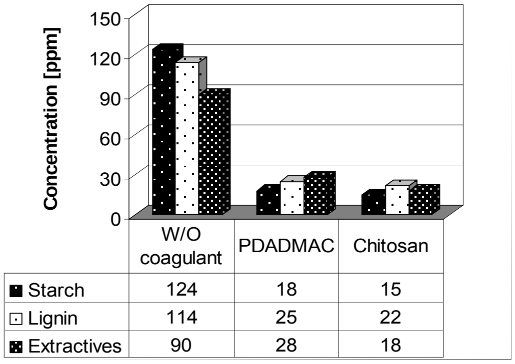


Figure 8: Effect of coagulants on accumulation rate of polysaccharides



	W/O coagulant	PDADMAC	Chitosan
■ Starch	124	18	15
□ Lignin	114	25	22
▨ Extractives	90	28	18

Figure 9: Comparative levels of starch, lignin and extractives after 10 recycling cycles

Generally, the data of Table 2 confirm the colloidal behaviour of the two chemicals, which induce intense coagulation phenomena with very positive effects on the wet-end processes. Chitosan is more effective when added to pulp suspension, an effect reported by other studies as well,[31,32] while PDADMAC shows a slightly higher coagulation rate for the CDM of process water. A better effectiveness of chitosan under real papermaking conditions could be explained by its special affinity for cellulose fibres, which can involve the formation of chitosan-CDM complex on the fibre surface. This mechanism and the ability of chitosan to develop hydrogen bonds could explain the improvement of the drainage rate and paper strength. At the same time, the complexation of colloidal compounds on the fibre surface involves a higher retention of AKD and respectively, the improvement of the sizing degree.

CONCLUSIONS

The present study evaluated the polyelectrolyte behaviour of chitosan by analyzing its interactions with anionic polymers and anionic colloidal compounds of wet-end papermaking systems and its effects on the processes of papermaking and paper properties.

The study on the interactions between chitosan and two different anionic polymers (CMC and PAA) demonstrated the ability of chitosan to form polyelectrolyte complexes (PEC), which was confirmed by its interaction with CDM of the papermaking process water. In the latter case, chitosan proved its coagulant properties by the precipitation and separation of the CDM from process water, its effectiveness being comparable with that of PDADMAC, but higher than that of PEI, which is currently used as a coagulant/flocculant for wastewater treatment.

Chitosan was more effective than PDADMAC when it was introduced into the papermaking stock, under conditions simulating short circuit of paper machine. Process water analysis evidenced that constant dosage of chitosan for 70% anionic charge neutralization results in consistent reduction of the CDM accumulation in process water, and especially of disturbing substances, such as starch, lignin and extractives.

Other important effects of chitosan as a wet-end additive include the improvement of the drainage rate, AKD sizing efficiency and tensile strength of paper sheets. The results of the study could suggest that the addition of chitosan to pulp suspension favours the interaction of chitosan with the CDM and complexes forming on the fibre surface. This type of hetero-coagulation can explain the positive impact on the drainage rate, on the retention of fines and additives, as well as on paper strength.

ACKNOWLEDGEMENTS: This paper was supported by the PERFORM-ERA "Postdoctoral Performance for Integration in the European Research Area" (ID-57649) project, financed by the European Social Fund and the Romanian Government (grant awarded to Dr. Raluca Nicu).

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