

# Adsorption and Complexation of Chitosan Wet-End Additives in Papermaking Systems

Houbin Li, Yumin Du, Yongmei Xu

Department of Environmental Science, Wuhan University, Wuhan 430072, China

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**ABSTRACT:** The adsorption of several chitosan samples with different degrees of deacetylation (65, 73, 85, and 92%) and their interactions with the main components of reed pulp suspensions were investigated with gel permeation chromatography, phenol/sulfuric acid spectrophotometry, microelectrophoresis, and retention/drainage methods. The results showed that the chitosan additive was almost completely adsorbed onto the surfaces of the cellulosic fibers, especially onto the surfaces of fines in a variety of cellulosic systems at low dosages corresponding to those used in industrial operations. This adsorption increased as the degree of deacetylation of chitosan increased. Moreover, the aggregation of the fine cellulosic particles was maximum at

a dosage of about 10 mg/kg of chitosan. The uptake of dissolved and colloidal carbohydrates always occurred in the cellulose suspensions upon the addition of chitosan. These phenomena were related to the maximum retention of fines and drainage performance of the pulp suspensions; the optimum drainage dosage was found to be about 5–8 mg of chitosan per gram of oven-dried pulp. The interactions between chitosan and the cellulosic substrates were dominated by a bridging mechanism at  $\text{pH} \approx 7$  for these experiments. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2642–2648, 2004

**Key words:** additives; adsorption; association; polyelectrolytes

## INTRODUCTION

A wet-end additive of papermaking should possess certain features. For example, it should be compatible with the cellulosic surface so that it does not disrupt the hydrogen bonding between celluloses; it should strongly interact with the cellulosic substrates so that retention is efficient; and it should be biodegradable, nontoxic, and environmentally clean. Such needs are met by chitosan, a linear copolymer containing a mixture of  $\beta$ -(1,4)-2-acetamido-2-deoxy-D-glucopyranose units and  $\beta$ -(1,4)-2-amino-2-deoxy-D-glucopyranose units, their ratio being dependent on the source of the polymer.<sup>1,2</sup> In addition, chitosan is antibacterial and renewable and is the second most widespread natural polysaccharide. The presence of a basic group ( $-\text{NH}_2$ ) transforms it into a polycation in a dilute acidic solution, and this cationic character should make it more strongly adsorbed on to an anionic pulp by electrostatic interactions. Therefore, chitosan may be a potential wet-end functional additive in papermaking.<sup>3,4</sup> So far, many attempts have been made to improve the papermaking process<sup>5,6</sup> and the properties<sup>7–9</sup> of paper upon the addition of chitosan, but some of these studies were performed at chitosan concentrations much

higher than those encountered in industrial applications.<sup>7,9</sup> In addition, fundamental studies of the adsorption phenomena and the interactions between paper components, which are related to the development of the properties of the final product (paper sheets), are still not reported. Therefore, the objectives of this study were to investigate the adsorption of several homogeneous deacetylated chitosans on various cellulosic substrates (cellulosic fibers and fines) and the interactions of chitosan additives with colloidal materials (e.g., cellulose fine) and soluble carbohydrates (e.g., dissolved hemicellulose and monomeric glucose) with gel permeation chromatography (GPC), phenol/sulfuric acid spectrophotometry,  $\zeta$ -potential measurements, and fines-retention and drainage methods. In this way, we could obtain a better understanding of the aggregation and uptake phenomena taking place at concentrations representative of those found in industrial papermaking systems.

## EXPERIMENTAL

### Chitosan

A commercial chitosan (Zhejiang Yuhuan Ocean Biochemistry Co., Ltd., Zhejiang, China) was dissolved in aqueous 1% (w/w) acetic acid; after filtration, the filtrate was neutralized with aqueous 4% (w/w) NaOH. The precipitate was collected and washed thoroughly with hot distilled water, ethanol, and acetone. The purified chitosan was obtained through dry-

Correspondence to: Y. Du (duyumin@whu.edu.cn).

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ing; its molecular weight<sup>10</sup> was around  $5.5 \times 10^5$ , and the degree of deacetylation (DD) was calculated to be 65% from the carbon and nitrogen contents with the following equation:<sup>11</sup>

$$DD = 1 - [(W_C/W_N - 5.14)/1.72] \times 100\% \quad (1)$$

where  $W_C/W_N$  is the ratio of carbon to nitrogen. This chitosan sample was homogeneously deacetylated,<sup>12</sup> and three other samples (DD = 73, 85, or 92%) were obtained. These four chitosan samples were dissolved in 0.2 mol/L acetic acid and 0.1 mol/L sodium acetate. All chitosan solutions were freshly prepared at 0.5% (w/w) to avoid any possible degradation.

### Cellulosic substrates

Bleached reed pulp (substrate content = 0.65%) was beaten to 76°SR (Schopper-Riegler degree) in a Valley beater (Northwest Light Industry Institute) to increase the specific surface area of the fibers before the addition of additives. The unwashed pulp was a typical pulp containing fibers, fines, and related dissolved and colloidal carbohydrates; coarse fibers and fines were separated by a 200-mesh screen from the unwashed pulp suspension. Suspensions of fines were used directly in the experiments, but the coarse fibers were thoroughly washed and screened with distilled water to get washed pulp. Another fraction of the unwashed pulp was alkali-treated with aqueous 10% (w/w) sodium hydroxide for 4 h at 35°C; after centrifugation, the precipitates were thoroughly washed and screened with distilled water until a neutral pH was achieved. This pulp is called alkali-treated pulp. The supernatant was neutralized with acetic acid, and the filtrate was treated with ethanol to produce hemicellulose.<sup>13</sup> For simplicity, these precipitates are denoted hemicellulose-I and hemicellulose-II, respectively.

Microcrystalline cellulose (MCC; 16- $\mu$ m average particle size) was thoroughly washed before being used.

All the suspensions of fiber pulp and fines were stored under refrigeration (4°C).

### Adsorption experiments

Stock solutions of chitosan (0.5 wt %) were added to aqueous cellulosic suspensions (pH  $\approx$  6.6). The suspensions were gently stirred overnight with a magnetic stirrer at room temperature until adsorption equilibrium. So that the carbohydrate adsorption on the vessel surfaces would be minimized, the total mass of each suspension used in the adsorption experiments was kept constant. Centrifugation was used to collect the supernatant because carbohydrates (chitosan, hemicellulose, degraded cellulose, and sugar)

could be adsorbed by the filtration medium. The samples were centrifuged at 4700 rpm for 30 min.

### GPC quantitative analyses

The residual chitosan contents of the supernatants after equilibration of the aqueous cellulosic suspensions with each additive were measured by GPC on a high-performance liquid chromatography (HPLC) with a TSP P100 pump (Thermoquest, San Jose, CA) and a TSK G5000PW column (Tokyo, Japan). The eluant consisted of 0.2 mol/L  $\text{CH}_3\text{COOH}$  and 0.1 mol/L  $\text{CH}_3\text{COONa}$ , the flow rate was 1 mL/min, the column temperature was 30°C, and the eluant was monitored with an RI-150 refractive index detector (Thermoquest, San Jose, CA). All data provided by the GPC system were collected and analyzed with Jiangshen workstation software (Dalian, China).

### Phenol/sulfuric acid spectrophotometric methods

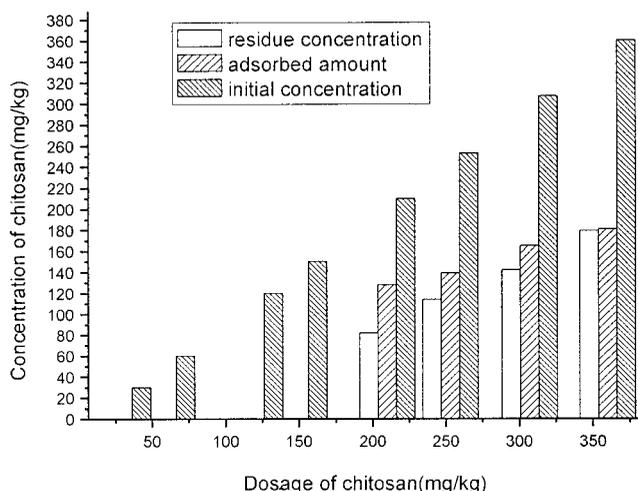
These were used to determine the total residual carbohydrate concentration<sup>14</sup> in the supernatant of aqueous pulp suspensions upon the addition of chitosan additives after adsorption equilibrium. The supernatant (4 mL), 0.2 mL of 80% distilled phenol, and 10 mL of concentrated sulfuric acid were subsequently added in a cuvette; after vigorous mixing, an amber color developed. The absorbance of the color solution at 490 nm was measured with a model 1601 ultraviolet-visible spectrophotometer (Shimadzu, Japan) zeroed by the substitution of pure water for an unknown sample.

### $\zeta$ -potential measurements

These were used to estimate the effect of chitosan on the charge of the systems.<sup>15</sup> The  $\zeta$ -potential values of fine particles in suspensions of fines upon the addition of chitosan were determined with a model BDL-B microelectrophoresis apparatus (Detecting Instrument Factory, Shanghai Detecting Technology Institute, China).

### Retention of fines and drainage performance

These were measured to correlate the chitosan adsorbed to the degree of colloidal retention of fine particles in the pulp suspensions. In industrial operations, the °SR value indicates the efficiency of the filtration performance of pulp suspensions. When the °SR value is low, the drainage of the pulp suspension is good. This indicates that the colloidal fines associate into large flocs. In the study reported here, a chitosan additive (DD = 85%) was added to 1000 mL of an unwashed pulp suspension containing 2 g of oven-dried pulp; after vigorous mixing, the °SR values were



**Figure 1** Effect of the chitosan dosage (DD = 85%) on the residual concentration and adsorbed amount of chitosan for unwashed pulp (the dosage is expressed as milligrams of chitosan per kilogram of the unwashed pulp suspension).

measured with a Schopper–Riegler J-DJY100 beating degree tester with a 200-mesh screen (Northwest Light Industry Institute).<sup>16</sup>

## RESULTS AND DISCUSSION

### Adsorption and aggregation in pulp suspensions

The residual chitosan concentrations in the supernatant of unwashed pulp suspensions upon the addition of chitosan with DD = 85% at various dosages were examined by GPC analysis; the concentrations versus the dosage are plotted in Figure 1. The residual chitosan concentrations in the supernatant of unwashed pulp suspensions were below the detection limit upon the addition of chitosan at dosage levels of less than 150 mg/kg, despite its sensitivity to 50 mg/kg in aqueous chitosan under the same conditions. Therefore, the added chitosan almost completely adsorbed onto the cellulosic substrate surfaces at low dosage levels. However, chitosan molecules were present in the supernatant of the pulp suspensions at high dosage levels. The amount of chitosan adsorbed ( $C_a$ ) by the cellulose substrates is also depicted in Figure 1.  $C_a$  was determined as follows:

$$C_a = C_i - C_r \quad (2)$$

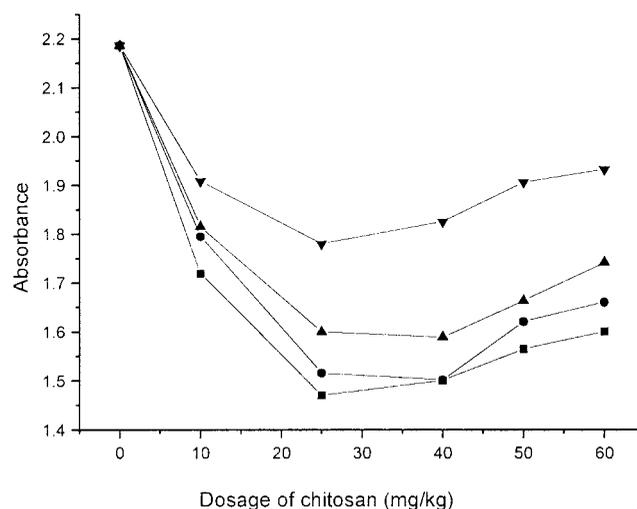
where  $C_i$  is the initial concentration of chitosan and  $C_r$  is the residual concentration of chitosan.

Comparing the trend of the residual chitosan concentration with that of the adsorbed amount of chitosan as the chitosan dosages were increased, we found that the former increased more steeply than the latter, and so the majority of the chitosan was incompletely adsorbed onto

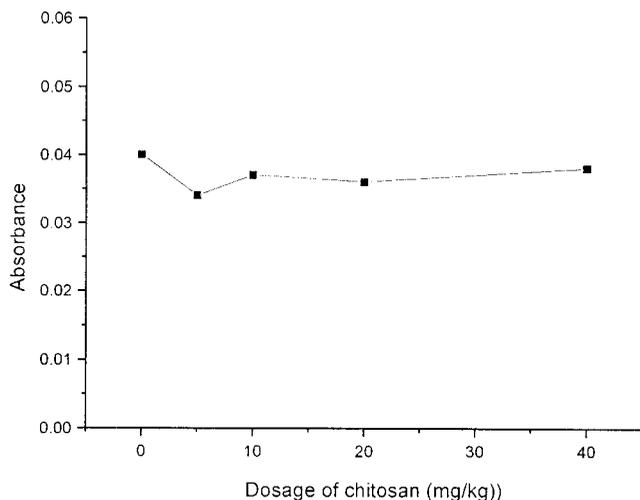
the cellulose surfaces at high dosage levels. Presumably, as a wet additive, the dosage of chitosan is always at a low level in industrial applications.

Figure 2 presents absorbance curves of the supernatant of unwashed pulp suspensions upon the addition of chitosan with different DD values (65, 73, 85, and 92). The curves show similar trends: the absorbance of the supernatant was reduced and then was minimum as the chitosan dosage was increased because chitosan was not only adsorbed onto the surfaces of fibers and fines but also formed complexes with soluble and colloidal carbohydrates (e.g., hemicelluloses and oligomeric sugars) in the pulp suspensions by hydrogen bonding, electrostatic interactions, van der Waal forces, and so forth. Therefore, the total polysaccharide (cellulose and chitosan) concentration of the supernatant upon the addition of chitosan was reduced, and the absorbance of the supernatant was reduced. However, when the dosage of added chitosan was high, the residual concentration of chitosan, as discussed earlier, was high because of incomplete adsorption. In addition, the system used here was a weak acidic solution; as a result of the increasing charge density of chitosan at a lower pH, the adsorption was so strong that the cellulosic substrate surfaces, especially fines and hemicellulose, developed a reversal of the sign of the surface charge. This overcompensated charge of cellulose surfaces, as shown later, led cellulose particles to restabilization, and the supernatant had high absorbance. This phenomenon was also in agreement with theoretical predictions.<sup>17</sup>

Furthermore, DD of the chitosan markedly affected the absorbance of the supernatant (see Fig. 2). The absorbance of the supernatant of an unwashed pulp suspension was low at the same chitosan dosage as



**Figure 2** Effect of the chitosan dosage on the absorbance for an unwashed pulp suspension: (■) DD = 92%, (●) DD = 85%, (▲) DD = 73%, and (▼) DD = 65%.



**Figure 3** Effect of the chitosan dosage (DD =85%) on the absorbance for a washed pulp suspension.

DD of the chitosan increased. With increasing deacetylation, the segments of chitosan contained more  $\text{—NH}_2$  and less  $\text{—NHCOCH}_3$ . This occurred as follows. First, the hydrogen-bonding interactions between the segments of chitosan and the cellulosic surfaces increased because of increasing  $\text{—NH}_2$  in the chitosan molecule. Second, the intermolecular hydrogen-bonding interactions between acetamido ( $\text{—NHCOCH}_3$ ) and hydroxymethyl ( $\text{HOCH}_2\text{—}$ ) moieties decreased, and the backbone of the chitosan molecule became more flexible. Both of these promoted strong absorption of chitosan onto the cellulosic substrate surfaces; therefore, at the same chitosan dosage, the absorbance of the supernatant of pulp treated by high-deacetylation-degree chitosan was lower than that of the supernatant of pulp treated by low-deacetylation-degree chitosan.

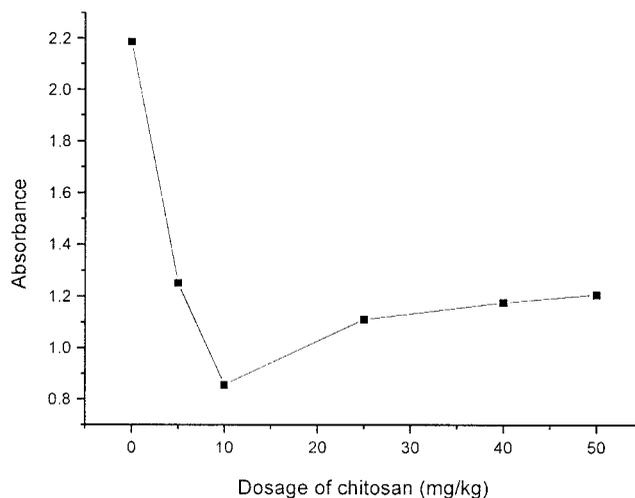
Figure 3 presents an absorbance curve of the supernatant of washed pulp suspensions upon the addition of chitosan (DD =85%). The absorbance trend was clearly no longer the same as it was in the unwashed pulp suspension. In this case, it was nearly horizontal because of a minimum of dissolved and colloidal carbohydrates as well as cellulosic fines. Therefore, no carbohydrate aggregation occurred in this system, and we can conclude that chitosan additives (up to 40 mg/kg) were completely adsorbed onto the surfaces of the cellulosic fibers.

In contrast to the washed pulp, there was appreciable carbohydrate aggregation upon the addition of chitosan to the suspensions of fines (Fig. 4). Large flocs were observed directly in the experiments. Although the absorbance trend was very similar to that in unwashed pulp suspensions (Fig. 2), the minimum value of the absorbance was lower, the relative dosage of chitosan was lower, and the absorbance curve was steeper in Figure 4 because chitosan was adsorbed

partly on the coarse fibers and partly on the other substrates (e.g., the cellulose fines). Comparing the added dosage of chitosan and the concentration of the cellulose substrates at the minimum absorbance in an unwashed pulp system with those in suspensions of fines (the optimum wet-end-additive dosage in an unwashed pulp suspension was ca. 35 mg/kg, and the optimum flocculation concentration was ca. 10 mg/g), we can conclude that the chitosan was more easily adsorbed by the surfaces of the particles of fines than by the surfaces of the coarse fibers. This agrees with the idea that the fine particles, to the best of our knowledge, had greater Brunauer-Emmett-Teller (BET) surface areas and higher surface charges than the coarse fibers in these experiments.

### Complex of chitosan with soluble carbohydrates

To further understand the interactions of chitosan additives with hemicellulose and monomeric glucose, which are often present in unwashed pulp suspensions, and the effects of the physicochemical characteristics of cellulosic surface on carbohydrate uptake, we first prepared hemicellulose and hemicellulose with unwashed pulp suspensions<sup>18</sup> and then used MCC, which is commonly used to simulate cellulosic fines, and alkali-treated pulp to investigate the absorbance of the supernatant. The experimental methods were the same as those in the suspensions of unwashed pulp or fines, except for the addition of hemicellulose and glucose (the hemicellulose and glucose concentrations were 2<sup>19</sup> and 1% with respect to the o.d. pulp, respectively). Tables I-III show the effects of chitosan (DD =85%) at a low dosage level (2 mg/g of chitosan/g of o.d. pulp) on the absorbance of each supernatant. The hemicellulose and glucose clearly were



**Figure 4** Effect of the chitosan dosage (DD =85%) on the absorbance for a fine suspension.

**TABLE I**  
Absorbance of the Supernatant of MCC and Alkali-Treated Pulp Suspensions with Hemicellulose I (H—I) on the Addition of Chitosan (DD = 85%)

	Substrate suspension	
	MCC	Alkali-treated pulp
Chitosan only	0.035	0.035
H-I only	0.031	0.031
Substrate only	0.062	0.078
Substrate + H—I	0.081	0.082
Substrate + H—I + chitosan	0.071	0.070

not completely adsorbed onto the cellulosic surfaces. It was also obvious that the absorbance of the supernatant for the MCC or alkali-treated pulp with hemicelluloses was markedly reduced as chitosan was added. Therefore, either hemicellulose or hemicellulose formed complexes with polysaccharide additives and then were retained on the substrate surfaces. Such behavior often occurs in the wet end of papermaking operations, that is, the uptake of dissolved and colloidal carbohydrates. Rojas and Neuman<sup>20</sup> and Keen and Opie<sup>21</sup> found the same physicochemical phenomenon when they studied the interactions between pulp suspensions and guar gum or cationic starch. This physicochemical phenomenon improves the strength and formation of paper.

However, Table III indicates that the absorbance of the supernatant for the system containing glucose was not reduced by the presence of chitosan. It was concluded that the uptake of glucose by the chitosan additive was negligible. In other words, glucose was averse to forming complexes with the additives. Presumably, this phenomenon was the reason that the absorbance of the supernatant was always greater than zero upon the addition of chitosan (see Figs. 2 and Fig. 3).

### $\zeta$ -potential, retention of fines, and drainage performance

Figure 5 shows the effects of chitosan (DD = 85%) on the  $\zeta$ -potential of the fine particles. The  $\zeta$ -potential of

**TABLE II**  
Absorbance of the Supernatant of MCC and Alkali-Treated Pulp Suspensions with Hemicellulose II (H—II) on the Addition of Chitosan (DD = 85%)

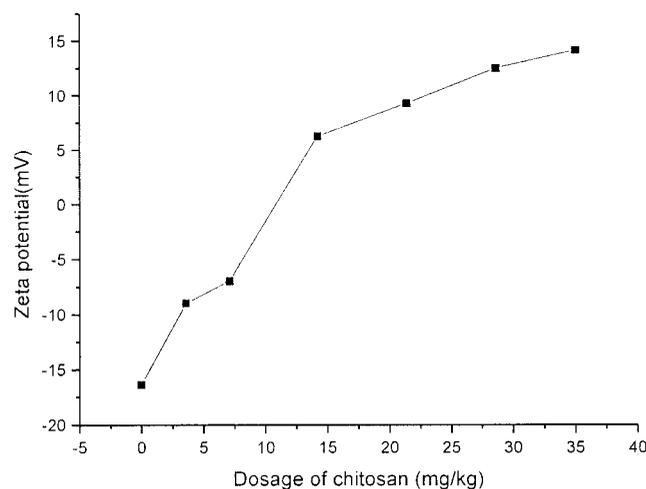
	Substrate suspension	
	MCC	Alkali-treated pulp
Chitosan only	0.035	0.035
H-II only	0.041	0.041
Substrate only	0.062	0.078
Substrate + H—II	0.085	0.083
Substrate + H—II + chitosan	0.062	0.054

**TABLE III**  
Absorbance of the Supernatant of MCC and Alkali-Treated Pulp Suspensions with Glucose (G) on the Addition of Chitosan (DD = 85%)

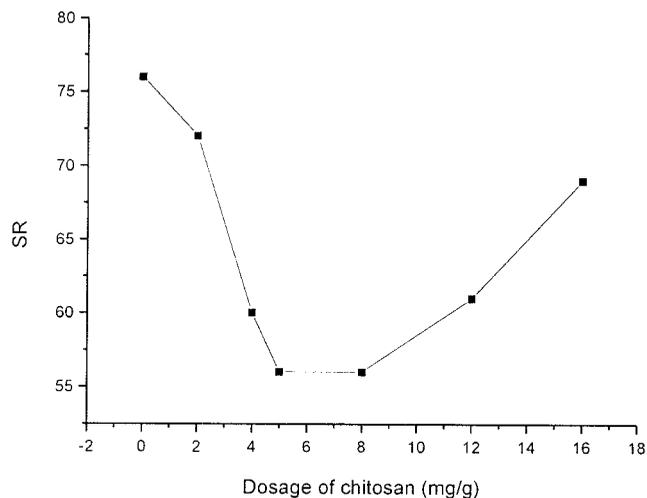
	Substrate suspension	
	MCC	Alkali-treated pulp
Chitosan only	0.035	0.035
G only	1.003	1.003
Substrate only	0.062	0.078
Substrate + G	1.060	1.072
Substrate + G + chitosan	1.092	1.102

the fine particles was 0 when the dosage of chitosan was around 11 mg/kg. This result was in excellent agreement with the minimum absorbance (ca. 10 mg/kg) of the supernatant of a suspension of fines (Fig. 4). Theoretically, the maximum retention of fines and best drainage performance occurred at this point. Nevertheless, an optimal  $\zeta$ -potential value cannot be drawn at a zero potential in industrial practice because of the intricate systems; many factors, such as the additive type, molecular weight, charge density, physicochemical properties of the fibers, and cost, must be considered. The  $\zeta$ -potential value, therefore, is generally in the vicinity of 0 (0 to -8 mV).<sup>20</sup> Because of the  $pK_a$  value (6.9)<sup>22</sup> of the glucosamine segments, the effects of chitosan on the charge of the fine particles at a pH of approximately 7 were less than those at a low pH<sup>23</sup> and those of quaternary chitosan.<sup>24</sup>

Figure 6 shows the drainage performance of unwashed pulp suspensions upon the addition of chitosan (DD = 85%). It decreased, and then a minimum in the °SR value could clearly be observed; this trend corresponded to that of the adsorption experiments and  $\zeta$ -potential results. When added at a low dose, chitosan was adsorbed onto the surfaces of the cellu-



**Figure 5**  $\zeta$ -Potential of a fine suspension upon the addition of chitosan (85%).



**Figure 6** Retention of fines and drainage for an unwashed pulp suspension upon the addition of chitosan (DD =85%; the dosage is expressed as milligrams of chitosan per gram of o.d. pulp).

losic substrates, and the fines were associated or aggregated into flocs. As the chitosan dose increased, this aggregation was more obvious, and the flocs were larger; therefore, the °SR value of the pulp suspensions decreased. When the aggregation was maximum, the °SR value was minimum, and the relative dosage was called the optimum drainage dosage. Figure 6 shows that the optimum drainage dosage was about 5–8 mg of chitosan/g of o.d. pulp. This dosage level was in good agreement with the minimum residual carbohydrate concentration (ca. 35 mg of chitosan/kg of unwashed pulp suspension, i.e., 5 mg of chitosan/g of o.d. pulp) in unwashed pulp suspensions. Presumably, it also corresponded to the maximum fines-retention concentration. However, at high dosages of chitosan, cellulosic fibers, especially fines, as shown earlier, were overcompensated and became redispersions in pulp suspensions, and so the °SR value increased and the drainage of pulp suspensions decreased.

### Interaction mechanism

It is known that bleached pulp contains hydroxyl groups, carboxylic acid groups, and aldehyde groups, and so cellulosic substrates in the reed pulp are thought to be polyanions due to the dissociation of carboxylic acid groups. Chitosan, containing amino groups and hydroxyl groups, is a polycation in an acidic solution. Therefore, the possible modes of interactions between chitosan and cellulosic substrates are as follows:

- Hydrogen bonding. The surfaces of cellulosic substrates and chitosan segments have suitable hydrogen-bonding sites (hydroxyl group/hydroxyl

group and hydroxyl group/amino group), and so hydrogen bonding is likely to occur.

- Electrostatic interaction. Added to pulp suspensions, chitosan, a cationic polyelectrolyte, is adsorbed onto the negatively charged sites present on the various components of pulp suspensions.
- Van der Waals forces. Interactions usually attractive of a quantum mechanical nature that are always present in colloidal systems.
- Covalent bonding. Primary amino groups of chitosan react with aldehyde groups of cellulosic substrates to form imino bonds (e.g., Schiff bases).
- For aggregation or association, two common mechanisms by which an oppositely charged polymer destabilizes a colloidal dispersion are patch flocculation and interparticle bridging.

*Patch flocculation* refers to local charge reversal of the particle surface with an adsorbed oppositely charged polymer. These patches of excess positive charge are surrounded by areas of negative charge that represent the original particle surface. Particles with this patchy type of surface-charge distribution may interact in such a way that positive and negative patches come into contact, thereby developing a strong interaction. In general, polymers are polyelectrolytes with high charge densities and medial molar masses.<sup>25</sup>

*Interparticle bridging* refers to a situation in which an adsorbed polymer layer extends into a solution and overcomes the thickness of the electrostatic double layer of the particle; therefore, the adsorbed polymers extend to the surfaces of other particles and promote association or aggregation. Interparticle bridging can be achieved with uncharged and charged polymers.<sup>25</sup>

These interactions can be important in practice, and sometimes all of them operate simultaneously, but often one of them is dominant. Figure 2 shows that the optimum dosage of each chitosan sample was near the same value (35 mg/kg) because the chitosan molecules were of the same length, despite the different charge densities of the polyelectrolyte and chitosan. Therefore, it was concluded that the interactions between chitosan and cellulosic substrates were dominated by bridging at a nearly pH-neutral solution. The long-chain chitosan molecules, using their tail fractions, bridged several cellulosic particles,<sup>26</sup> forming large flocs that were easily separated from cellulosic suspensions by centrifugation. This was in agreement with theoretical predictions by Böhmer et al.,<sup>27</sup> who showed that bridging attraction increased at a low polyelectrolyte adsorption. It was also in line with a Monte Carlo simulation<sup>28</sup> that showed that bridging attraction was important between charged surfaces partly or fully neutralized by adsorbed polyelectrolytes, whereas bridging attraction was not important when the surface charge was strongly overcompensated by the adsorbed polyelectrolytes.

## CONCLUSIONS

On the basis of the adsorbed amount of chitosan, the residual carbohydrate concentrations of the supernatant, the  $\zeta$ -potential, and the results for fines-retention and drainage, chitosan interacted with each component (coarse fibers, fines, and soluble and colloidal carbohydrates) of reed pulp suspensions at very low dosages, which were representative of those found in industry. That is, chitosan was adsorbed onto the surfaces of cellulose fibers, especially on the surfaces of particles of fines and colloidal carbohydrates, possibly by hydrogen bonding, electrostatic neutralization, van der Waals forces, and so forth. The polysaccharide additive also aggregated or associated the fine particles through bridging attraction. In addition, the adsorption and aggregation behaviors were clearly affected not only by the surface physicochemical properties of the cellulosic substrates but also by the nature (e.g., DD) of chitosan. That is, the interactions between chitosan and cellulosic substrates increased as the degree of deacetylation of chitosan or the BET surface area of cellulosic substrates increased. The carbohydrate uptake of soluble hemicellulose by chitosan obviously occurred, and this was then retained on the fibers. Presumably, these phenomena were related to the maximum retention of fines and drainage aid as well as the paper strength.

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