

# The Interface Interaction Between Water-Soluble Chitosan (DD = 50%) and Peroxide Bleached Reed Kraft Pulp

Wenjuan Gu,<sup>1</sup> Houbin Li,<sup>1,2</sup> Huaiyu Zhan,<sup>2</sup> Jun Ding,<sup>3</sup> Xiaohui Zhang<sup>1</sup>

<sup>1</sup>Pulping and Papermaking Department, School of Printing and Packaging, Wuhan University, 430072 Wuhan, China

<sup>2</sup>State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, 510640 Guangzhou, China

<sup>3</sup>Department of Building and Information Engineering, Shandong Vocational College of Industry, 256414 Zibo, China

Received 6 August 2010; accepted 16 December 2010

DOI 10.1002/app.33990

Published online 24 March 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** The adsorption and the interactions of water-soluble chitosan (DD = 50%) with main components of reed pulp suspensions were investigated with phenol/sulfuric acid spectrophotometry, microelectrophoresis, and retention/drainage methods. The results showed that the Zeta potential of peroxide bleached reed kraft pulp transformed from negative to zero and then to positive because of the adsorption of water-soluble chitosan. Nonelectrostatic forces (hydrogen bonding, Van der Waals force) existed between the fibers and water-soluble chitosan; electrostatic force existed between cellulose fines and water-soluble chitosan. The experimental results showed that the fines existed in pulp suspension would aggregate upon the addition of water-soluble chitosan. The degree of flocculation

was affected by the type of cellulose substrates, the electrolyte concentration and pH in the background. With the increase of NaCl concentration, the flocculation performance of water-soluble chitosan decreased slightly for unwashed pulp, whereas the flocculation efficiency of water-soluble chitosan decreased significantly for fine suspension. These adsorption and flocculation resulted in excellent drainage performance of reed pulp, for example, the <sup>0</sup>SR of cellulosic pulp was reduced by about 39 or 18% at  $C_{\text{NaCl}} = 0$  mol/L, at pH 5 or pH 7, respectively. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2606–2613, 2011

**Key words:** adsorption; water-soluble chitosan; interface interaction; wet-end additives; zeta potential

## INTRODUCTION

Every wet-end additive of papermaking should possess certain features. For example, it should be compatible with the cellulosic surface so that it would not disrupt the hydrogen bonding among celluloses; it should interact strongly with the cellulose substrates thereby the retention is efficient; and it should be nontoxic, and environment friendly. 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,<sup>1</sup> could meet all these needs. In addition, chitosan is antibacterial and renewable. The presence of the basic group ( $-\text{NH}_2$ ) transforms chitosan into a polycation in dilute acidic solution. This property could make it be adsorbed onto anionic pulp more strongly by electrostatic force.<sup>2</sup> Therefore, chitosan

could be used as 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 of paper upon the addition of chitosan. But the chitosan concentrations in most of the reported studies were higher than those applied in industrial process. In addition, fundamental studies on the adsorption phenomena and the interactions between paper components, which are related to the properties of the final product (paper sheets), still have not been reported to our knowledge. The objective of this article was to investigate the adsorbed amount of water-soluble chitosan with degree of deacetylation of 50% (DD = 50%) on cellulose substrates (cellulose fibers and fines). Furthermore, the interactions of chitosan additives with colloidal materials (e.g., cellulose fines) and soluble carbohydrates (e.g., dissolved hemicellulose and monomeric glucose) were also investigated by phenol/sulfuric acid spectrometry, fines-retention and drainage methods, and  $\xi$ -potential measurements. In this way, we could obtain a better comprehension of the aggregation and the phenomena taking place at several representative concentrations of those applied in industrial papermaking systems.

As an additive in wet-end of papermaking system, chitosan is generally suitable for the relatively

Correspondence to: H. Li (lhb@whu.edu.cn).

Contract grant sponsor: Independent Research Projects of Wuhan University; contract grant number: 5081001.

Contract grant sponsor: Doctor's Independent Research of Wuhan University; contract grant number: 20082170201000053.

outdated production technology system (acidic papermaking system). It has been reported that chitosan can improve the dry and wet strength of the handsheet substantially in alkaline conditions. But it makes no change in the dewatering of the pulp and the retention of fine fibers. With the development of paper-making system, transferring gradually from acidic to neutral and alkaline, it becomes inconvenient to use regular chitosan in this specific paper-making process. Because regular chitosan cannot be dissolved in the neutral and alkaline condition. So there would be neither flocculation nor dewatering of reed pulp by chitosan. Nishimura and his co-workers<sup>7</sup> have reported that chitosan (DD = 50%) could be dissolved in alkaline medium. Hence, it can be applied to neutral and alkaline paper-making systems. However, to our knowledge, study on chitosan (DD = 50%) used as functional additive in papermaking has not been reported until now.

This work focused on the inspection of physical and chemical interactions between the water-soluble chitosan (DD = 50%) and cellulose fibers, fine fibers, or soluble carbohydrates. The possible mechanism between reed pulp and chitosan as wet-end functional additive in papermaking was brought forward in this report.

## EXPERIMENTAL

### Materials

**Chitosan:** produced by Zhejiang Yuhuan Ocean Biochemistry Co. (Zhejiang, China). Its degree of deacetylation was determined to be 85% by a potential titration method,<sup>8</sup> and its molecular weight was about  $3.0 \times 10^5$  measured by GPC method.<sup>9</sup>

**Cellulose substrates:** Peroxide bleached reed kraft pulp (substrate content of 0.5%, w/w) was provided by Chenming Papermaking Co., (Wuhan, China). The pulp was first treated by HCl (pH 2) to wipe off the little metal ions adsorbed on the fibers. Then it was washed to neutral and beaten to 43<sup>0</sup>SR (Shopper-Riegler beating degree) afterward in a Valley beater.

'Unwashed pulp' was a typical pulp containing fibers and fines. The fibers and fines were collected after being separated by 200-mesh screen from the 'unwashed pulp' suspension. 'fine suspension', containing fines and colloidal substances, were used directly without examining the substrates content in the experiments. The separated fibers were thoroughly washed and screened with doubly distilled water to get 'washed pulp'. All the suspensions of fiber pulp and fines were stored under refrigeration (4°C).

**Acid Orange:** (C.I. Acid Orange 7), spectral pure, was purchased from Huamaolong Technology Co.

(Tianjin, China). Other chemical reagents are all analytically pure.

## METHODS

### Preparation of water-soluble chitosan

The water-soluble chitosan was prepared as follows according to reference.<sup>7</sup> First, 0.3 g Chitosan (DD = 90%) was added to the mixture of 8 mL of 10% acetic acid and 8 mL methanol. Then the resulting solution and 0.93 mL acetic anhydride were poured into 100 mL pyridine. Water-soluble chitosan was obtained after reacting at room temperature for 5 h. Its molecular weight was about  $2.4 \times 10^5$  (by GPC<sup>9</sup> with water adopted as solvent) with the degree of deacetylation of 50% (measured by potentiometric titration<sup>8</sup>).

### Adsorption experiments

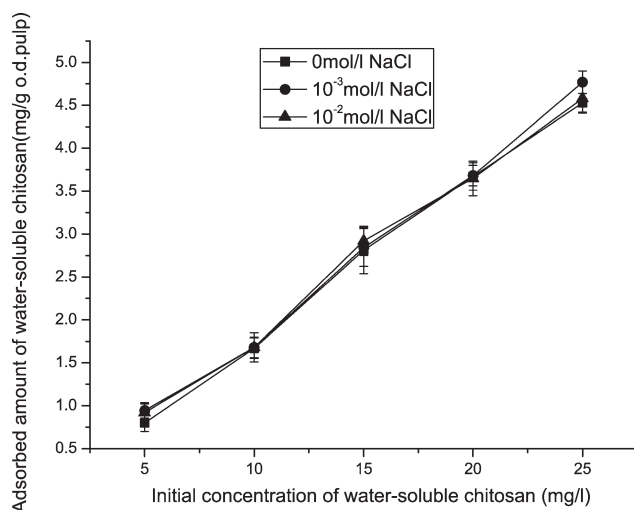
The cellulose suspension (pH 7) was added to stock solutions of chitosan (0.2% w/w). Then adsorption equilibrium was achieved after stirring the suspension gently overnight (around 20 h) with a magnetic stirrer at room temperature. The total mass of suspension used in adsorption experiments was constant to minimize the effect of carbohydrate adsorption on the vessel surface. As carbohydrates (polysaccharide additives, hemicellulose, degraded cellulose, and sugar) could be adsorbed by the filtration medium,<sup>10</sup> the supernatant was collected by centrifugation method. The Model LD5-10 was employed to centrifuge the samples at 4500 rpm for 30 min, and the supernatant was piped off to analyze.

### Adsorbed amount determination

The residual concentration of chitosan in the supernatant of aqueous pulp suspensions was estimated by C.I. Acid Orange 7 (15510) at adsorption equilibrium after the addition of chitosan.<sup>11</sup> That is, 10 mL of the supernatant was mixed with 1 mL of aqueous C.I. Acid Orange 7 ( $2 \times 10^{-4}$  w/w). The absorbance of the resulting solution at 484 nm was measured with the Model 1601 UV/vis spectrophotometer (Shimadzu, Japan). The residual concentration of chitosan in the supernatant of pulp suspension could be obtained from a calibration curve based on a known sample. Accordingly, the adsorbed amount ( $C_a$ ) of chitosan was calculated as follows:

$$C_a = (C_i - C_r) \times V/m \quad (1)$$

Where  $C_i$  is the initial concentration of chitosan,  $C_r$  is the residual concentration of chitosan,  $V$  is the



**Figure 1** Adsorbed amount of water-soluble chitosan onto the unwashed pulp as a function of electrolyte concentration at pH 7 and 20 °C.

volume of pulp dispersion,  $m$  is the weight of dried pulp.

#### Total residual carbohydrate concentration

There were adsorption equilibriums in the supernatant of aqueous pulp suspensions after the addition of chitosan. The total residual carbohydrate concentrations were determined by the phenol/sulfuric acid spectrophotometric method.<sup>12</sup>

First, 4 mL of the supernatant, 0.2 mL of 80% distilled phenol and 10 mL of concentrated sulfuric acid were subsequently added into a cuvette, stirring vigorously until amber color appeared. Then the absorbance of the solution at 490 nm was measured with the Model 1601 ultraviolet-visible spectrophotometer (Shimadzu, Japan), and pure water was used as blank.

#### Zeta potential

The Model BDL-B microelectrophoresis apparatus<sup>13</sup> (Detecting Instrument Factory, Shanghai Detecting Technology Institute, China) was employed to determine the Zeta potential values of the fine particles in fine suspensions. All suspensions upon addition of chitosan were gently agitated for 20 min, and then centrifuged for 2 min at 2000 rpm before being measured.

#### Drainage performance of pulp

To find the relation between the effect of polysaccharide adsorption with the drainage in the pulp suspension upon suppression of mechanical entanglement and the filtration effects that are commonly present during mat formation in paper manufacture,

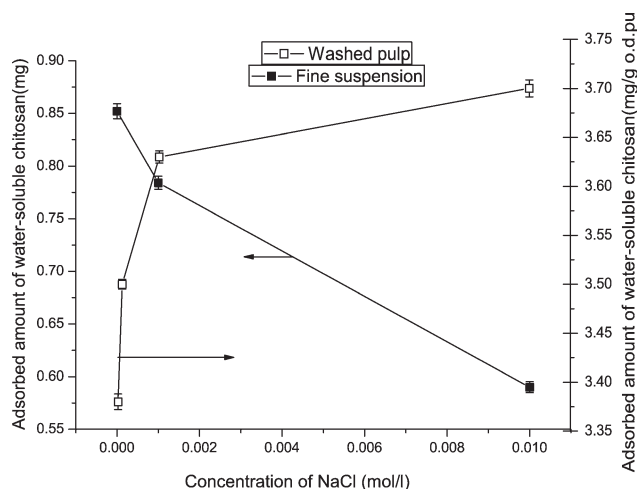
1000 mL of unwashed pulp suspension containing 2 g of dried pulp was added with chitosan. After stirring, the  $\theta$ SR values were measured with the Model ZDJ-100 beating degree tester (Second Materials Factory of Changchun, China) with a 200-mesh screen.

## RESULTS AND DISCUSSION

### The relationship between adsorbed amount of water-soluble chitosan and electrolyte concentration

The adsorbed amount of water-soluble chitosan changed with the electrolyte concentration in different pulp as shown in Figures 1, 2. From the figures we can easily see that the adsorbed amount of chitosan on unwashed pulp had no relationship to NaCl concentrations (0– $10^{-2}$  mol/L) (Fig. 1); it was obviously observed that the adsorption of chitosan on fine suspension gradually decreased with the increasing of NaCl concentration (Fig. 2); the adsorbed amount of chitosan on washed pulp increased with the increasing of the electrolyte concentration (Fig. 2). It can be inferred from these experimental phenomena that the interactions of the chitosan with various components of wet-end were different. That is, in fine suspension, the interaction between chitosan and cellulose substrates was dominated by the electrostatic force; in Washed pulp, the main interaction between the two parts were non-electrostatic forces, such as hydrogen bonding, Van der Waals force, etc.; but in unwashed pulp, the proportion of electrostatic force and nonelectrostatic force was similar.

On the basis of Van der Steeg<sup>14</sup> theory, the above conclusions could be explained as follows:



**Figure 2** Adsorbed amount of water-soluble chitosan onto fine suspension (fine suspension: 100 g; water-soluble chitosan: 1.5 mg) and Washed pulp as function of electrolyte concentration at pH 7 and 20 °C.

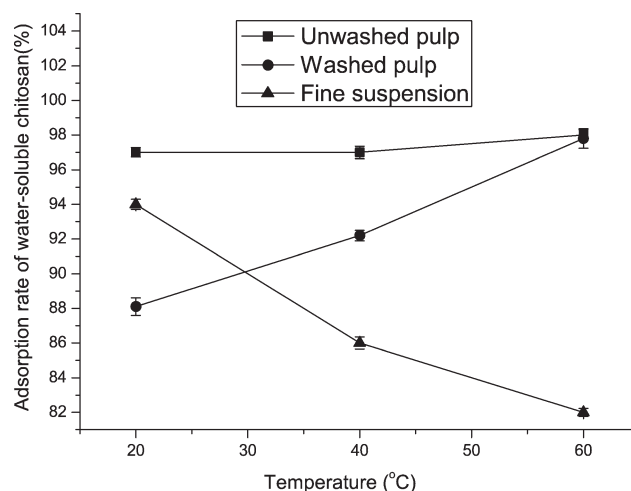
1. In fine suspension, cellulose substrates existed mainly in the form of fine fibers and colloidal carbohydrate. There were many carboxyl, sulfonic group, phenol hydroxyl group exposed outside, which caused the high potential on the surface. Therefore, the interaction between chitosan and cellulose was mainly electrostatic force. It is well known that, at high salt concentration, the range of the electrostatic interaction become smaller; i.e., the attraction between chitosan and surface is screened. Because the salt ions have a finite volume, the cations also competed with the chitosan for adsorption sites on the surface. The chitosan desorbs if the salt cations are more effective in compensating the surface charge. When the electrolyte was added, the cationic salt and chitosan competed for the negative charges on the surface of the cellulose substrates. As a result, the attraction between the chitosan chain and cellulose substrate was screened, which would reduce the adsorbed amount of chitosan. Polyacrylamide had the similar adsorption phenomenon when it was adsorbed on the surface of silica gel<sup>15</sup> or montmorillonite.<sup>16</sup>

2. In Washed pulp, the cellulose substrates were thick, the negative charge on the surface of these fibers was lower than those of the fines or colloidal carbohydrate. Hence, the interaction between fibers and chitosan were mainly hydrogen bonding, Van der Waals forces, and other nonelectrostatic forces. Naturally, at high salt concentration the repulsion is screened; hence they can adopt conformations with loops and tails, and the adsorbed amount increases. A fully screened polyelectrolyte can only adsorb if there is an attractive interaction between segments. So, at high electrolyte concentration, the screen of the repulsion between segments resulted in further forming of the chitosan chain ring and chain tail which caused the increase of the adsorbed amount.

3. Unwashed pulp system contained not only coarse fibers but also fines and colloidal carbohydrate. The proportion of the electrostatic force and nonelectrostatic force between these substrates and chitosan was similar. Thus, the adsorbed amount almost had no relation to the electrolyte concentration.

#### The relationship between adsorption rate of water-soluble chitosan and temperature

Temperature was an important parameter in the paper-making process as it restricted the adsorption process obviously. Adsorbed amount of chitosan in different pulp under 20, 40, and 60°C were shown in Figure 3. The results revealed that the adsorption rate of chitosan increased with the increasing of temperature in unwashed pulp and washed pulp. The increasing speed of adsorbed amount in Washed



**Figure 3** Adsorption rate of water-soluble chitosan onto the unwashed pulp, washed pulp, and fine suspension as a function of temperature (fiber suspension: 100 g; water-soluble chitosan: 5 mg; pH 7).

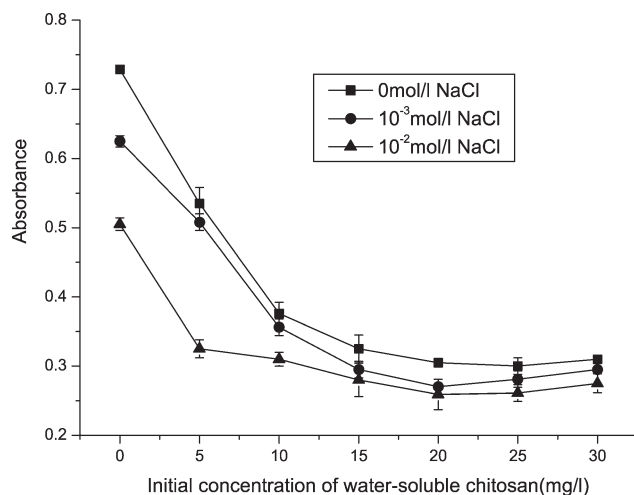
pulp was far higher than that in the unwashed pulp system. But the adsorption rate of chitosan decreased in fine suspension.

Generally, adsorption is a spontaneous process, that is  $\Delta G^0 < 0$ . At the same time, the entropy decreased in the adsorption process. According to  $\Delta G^0 = \Delta H^0 - T\Delta S^0$ , it could be easily inferred that the adsorption enthalpy ( $\Delta H$ ) was negative. Therefore, the adsorption enthalpy fell with the increase of the temperatures.

The above reasoning was based on the hypothesis that the adsorbate and adsorbent had no relation to the temperature, and the adsorbent's surface was clean. However, the actual adsorption was a complex process. The adsorption of polymer in the solution was decided by the interaction balance of three interactions between the polymer-solvent, the polymer-adsorbent and the solvent-adsorbent. Any change would inevitably affect these interactions, thus resulting in the change of adsorbed amount. Therefore, the caloric effect produced by adsorption of polymer on the solid surface was likely to be exothermic<sup>17,18</sup> or endothermic.<sup>19,20</sup>

Adsorption was an endothermic process for the Washed pulp, so the adsorbed amount increased with the increasing of temperature. As for the Fines, the adsorption enthalpy was negative, and the adsorbed amount decreased with the increasing of temperature. As unwashed pulp was composed of washed pulp and fine pulp, the adsorption was also an endothermic process, but the adsorption enthalpy was not as high as that of washed pulp. So the increasing speed of adsorbed amount in washed pulp was far higher than that in unwashed pulp with the increasing of temperature. The adsorption process of the cationic starch with different





**Figure 4** Effect of the water-soluble chitosan dosage on the absorbance for unwashed pulp as a function of electrolyte at pH 7 and 20 °C.

thermodynamic mechanical pulp (TMP) was affected by temperature in the same way as reported by Bobacka.<sup>21</sup>

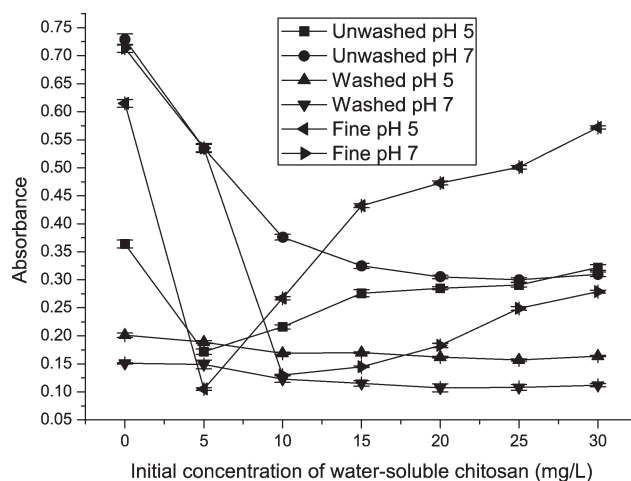
#### Effect of the electrolytes on the gathering of fibers

The gathering of the fine fibers could be explained by the adsorption of the polyelectrolyte on their surface. But the adsorbability could not determine the retention levels of the fines, especially for the polyelectrolyte with high charge density. Therefore, it would be a more reasonable method to determine its flocculation capacity indirectly by the total sugar content in the white water adsorption system.<sup>20</sup> Generally, the higher the sugar content in the white water system, the higher absorbency in spectrometer would be, which meant lower retention capacity of the retention aids. The effects of chitosan on the total concentration of sugar in different pulp were shown in Figures 4, 5. From Figure 4, it could be seen that the sugar concentration in the white water system decreased distinctively at low dose of chitosan. The total sugar content reached a minimum value when the chitosan concentration was 25 mg/L, after which there was a weak increase. This phenomenon could be explained that the adsorption of chitosan could bridge fines and made them flocculate at low dose, so the total sugar content decreased. When chitosan concentration was higher than 25 mg/L, the charge on the fines' surface would reverse to positive due to the relatively excessive adsorption of chitosan. This charge reversal phenomenon would lead to the increase of repulsion force between fines, and decreased the flocculation ability. Thus, the total sugar content in the white water system increased slightly. This phenomenon matched with the drainage properties mentioned later.

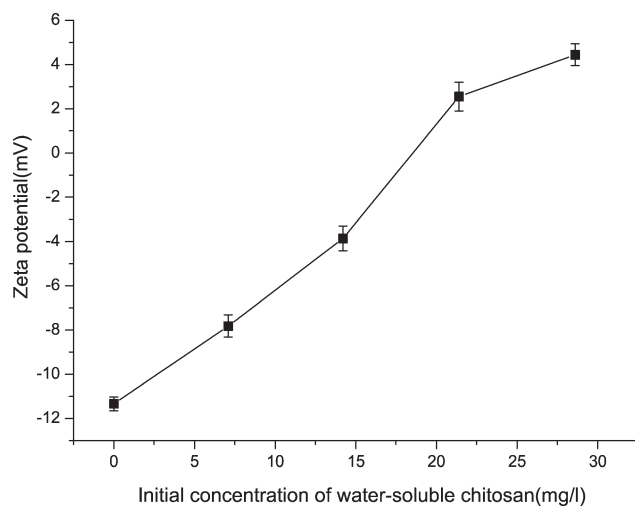
It could also be seen from Figure 4 that the higher the electrolyte concentration, the lower the sugar content in the white water system. The difference between the decline rate of total sugar content was not obvious. This was because of the thickness compression of the double layers caused by electrolyte on the fiber substrate surface. This result was in agreement with the phenomenon in the unwashed pulp system, in which the adsorbed amount of chitosan had no relation to the concentration of NaCl (shown in Fig. 1).

The effects of chitosan on the total sugar content in different pulp were shown in Figure 5. It was clearly shown that the sugar content of white water system in the unwashed pulp decreased at pH 7 after the addition of chitosan. But in washed pulp system, the sugar content was not affected by addition of chitosan, which was kept at a relatively low level. This difference was due to that there were many fine fibers besides cellulose fiber in unwashed pulp; while only a little fine fibers were maintained in the Washed pulp system, and thus the total sugar concentration in the white water was too low to flocculate.

The impact of chitosan on sugar content in fine suspension system at different pH was shown in Figure 5. In this system, the trends of the sugar content in white water were similar to those in Figure 4. With the increasing of chitosan concentration, the total sugar content decreased to a minimum value at 10 ~ 15 mg/L, after which it increased slightly. However, the optimum concentration of flocculation was different for different pulp. Taking the results at pH 7 for example, in fine suspension system it was 10 ~ 15 mg/L, whereas in unwashed pulp system it was 25 mg/L. In the fine suspension, the flocculation of fine particles was caused by chitosan. When the electrochemical dose of chitosan was higher than the



**Figure 5** Effect of the water-soluble chitosan dosage and pH on the absorbance for unwashed pulp, washed pulp, and fine suspension at 20 °C.



**Figure 6**  $\zeta$ -potential of fine suspension upon the addition of water-soluble chitosan at pH 7 and 20 °C.

cellulose substrate amount in fine suspension, it is easy for the fines to acquire excessive positive charges.<sup>22</sup> The deterioration of flocculation caused the increase of sugar content in white water. This phenomenon was more obvious at pH 5, as there was an inflection point when the concentration of chitosan was about 5 mg/L. The chitosan's positive charge density was higher at this point than that at pH 7. Therefore, the charge reversal was easy to take place, which was in agreement with the results of the unwashed pulp at different pH. For the unwashed pulp at pH 5, the excessive loading of chitosan on the surface would lead to the excessive positive surface charges, which strengthened the interaction of chitosan with the cellulose substrates. Therefore, the flocculation was enhanced and the total sugar content in the white water was decreased. It can be inferred from the above experimental results that chitosan (DD = 50%) could be applied to both acidic and alkaline paper-making system.

#### Effect of water-soluble chitosan on the potential of cellulose substrate surface

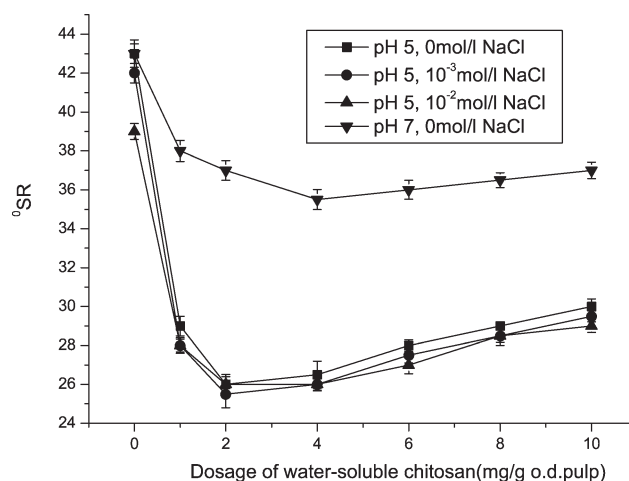
In the papermaking process, the potential of pulp surface was an important parameter. It determined the dewatering capacity and retention performance of pulp to a certain extent. Generally, the smaller repulsion among particles, the more retention; and the weaker hydration process, the higher dewatering speed. It could be inferred that  $\zeta = 0$  mV would be the optimum condition for flocculation. But there were high dewatering and retention efficiencies because of the effect of bridge interaction in the vicinity of neutral (0 ~ 8 mV) for some other systems.<sup>23</sup> The  $\zeta$ -potential of the fine suspension upon the addition of water-soluble chitosan at pH 7 was shown in Figure 6.

The experimental results showed that, with the increase of the chitosan dose, the  $\zeta$ -potential of the pulp changed gradually to positive. When water-soluble chitosan was around 16 mg/L, the potential of the pulp surface was about zero. The chitosan neutralized the negative charges in cellulose substrate surface at this point. This isoelectric point (16 mg/L) was higher than the optimum flocculation concentration (10 ~ 15 mg/L), as shown in Figure 5. It could be inferred that the water-soluble chitosan affected the flocculation of the reed pulp mainly by the bridge mechanism. Relatively small amount of long-chain chitosan molecules could make the flocculation reach its optimum condition before the reed pulp surface reached electricity neutrality. This result matched with theoretical predictions.<sup>24</sup>

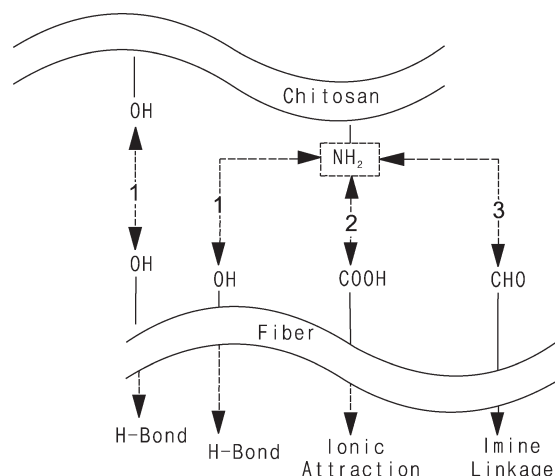
#### The drainage property of water-soluble chitosan

To understand the practicality of water-soluble chitosan as wet-end additive in paper-making, we investigated their dewatering properties. The dewatering of reed pulp in different pH, NaCl concentrations were shown in Figure 7. The results revealed that  $^0$ SR value of reed pulp decreased slightly when the concentration of electrolytes was increased. This phenomenon was in consistent with the results shown in Figures 1 and 4.

The  $^0$ SR value of pulp decreased with increase of water soluble chitosan dose at pH 7. It increased slightly after reaching the minimum value, shown in Figure 7, whose trend was similar to the flocculation results shown in Figure 4. However, it would be found that the chitosan doses were different to achieve the minimum  $^0$ SR (shown in Fig. 7) and the lowest sugar content (shown in Fig. 4). That was, the optimum dewatering concentration was 4 mg/g o.d.pulp, whereas the optimum flocculation concentration was



**Figure 7** Effect of the dosage of water-soluble chitosan on drainage for unwashed pulp suspension at different pH and electrolyte concentration.



**Figure 8** Interactions between chitosan and cellulosic fibers.

25 mg/L or 5 mg/g o.d.pulp. The reason for these differences was that the content of cellulose substrate was 0.5% in the adsorption experiment, whereas it was 0.2% in the dewatering experiment. Satao<sup>25</sup> found the same trend when he studied the adsorption of polyamide onto metal oxide pigments. And so did Hedborg when he<sup>26</sup> investigated the adsorption of cationic starch onto  $\text{CaCO}_3$  particles.

In addition, Figure 7 showed that the pH of the system affected drainage property of water-soluble chitosan greatly. The drainage properties of pulp suspensions were improved with the increasing of acidity. This could be explained as follows, the charge density of water-soluble chitosan was high at pH 5, and its interaction with cellulose substrate increased. Thus, its dewatering efficiency was the optimum when the charge density was about 3 mg/g o.d.pulp.

#### The interaction between Chitosan and cellulose substrate

Both the primary structure and the remote structure were similar for chitosan and cellulose, which resulted in good compatibility between them.<sup>1</sup> As shown in Figure 8, some interactions were certain existed between chitosan and fiber.

##### Hydrogen bonding

Chitosan molecule contained a large number of hydroxyl and primary amino groups, while cellulose molecules contained hydroxyl groups. All these groups could form intermolecular hydrogen bonding in the form of  $-\text{OH}-\text{NH}_2$ ,  $-\text{OH}-\text{OH}$ .

##### Ionic bond

Hemicelluloses in the pulp substrate contained glucuronic acid, as a certain amount of carboxyl

( $-\text{COOH}$ ) groups were introduced to the molecular chain after the pulp being bleached.<sup>27</sup> The  $-\text{NH}_2$  in chitosan molecules was alkaline group, so it would form an ionic bonding as  $-\text{NH}_3^+-\text{COO}^-$ , whose interaction would increase with the strengthening of the potential on the cellulose substrate surface. Unbleached pulp contained lignin phenolic hydroxyl groups, and certain amount of sulfonic groups introduced in the process of mechanical pulp sulfite treatment. These phenolic hydroxyl and sulfonic groups could also form ionic bond with  $-\text{NH}_2$ .

##### Covalent bond force

A small amount of  $-\text{CHO}$  were introduced into the molecular chain after cellulose molecules being bleached. These aldehyde groups could form Schiff bond with  $-\text{NH}_2$  in chitosan molecules.<sup>28</sup>

##### Van der Waals forces

In the pulp suspension, when the gap between the chitosan and other components was less than Van der Waals radius—the Van der Waals force—which was universal gravitation in all atoms, was the obvious interaction form. Its intensity depended on the polarity, size, contact area, deformation of the two sides, etc. For wet-end system in paper-making (colloidal dispersion), the Van der Waals force, which was in inverse proportion to the 6 power of distance in short distance, became very obvious.

The relative strength of the aforementioned forces was different. The interaction between chitosan and cellulose substrate was often controlled by one main force among them. Because the proportion of various forces was not only related to the type of pulp substrate, surface physical and chemical morphology—the properties of chitosan, such as molecular weight, the degree of deacetylation—but also related to the system condition such as pH, electrolyte concentration, etc. Therefore, the main force would be different under different conditions. From the discussion in this paper it can be easily seen that the proportion of electrostatic force in fine suspension was higher than that of nonelectrostatic force; nonelectrostatic force was stronger than electrostatic force in washed pulp system; and nonelectrostatic force was similar to electrostatic force in unwashed pulp system.

## CONCLUSIONS

The adsorption and flocculation behaviors which occurred in pulp suspension were affected not only by the surface physicochemical properties of cellulose substrates but also by background such as temperature, pH, and electrolyte concentration.

The adsorbed amount of water-soluble chitosan on unwashed pulp increased slightly with the increasing of temperature, but retained almost the same with the changes in ionic strength. The adsorbed amount of chitosan on fine suspension decreased with the increasing of temperature and ionic strength. However, the adsorbed amount of chitosan on washed pulp increased with the increasing of temperature and ionic strength.

Among the interactions between them, the non-electrostatic force was similar to the electrostatic force in unwashed pulp; whereas the main interaction between chitosan and fines was electrostatic force for fine suspension; and nonelectrostatic was the dominant force for washed pulp.

Chitosan can flocculate the cellulose substrate, especially fines, colloidal, and soluble carbohydrate. We investigated the adsorption and flocculation processes in different pulp. The optimum flocculent concentration was about 25 mg/L (5 mg/g o.d.pulp), which was similar to the best dewatering property (4mg/g o.d.pulp). On the basis of the results described above, it was concluded that water soluble chitosan (DD = 50%) was full of some promises as wet-end additive and could be used in paper-making production.

## References

1. Hudson, S. M.; Smith, C.; In: Kaplan, D. L., Ed.; Springer-verlag: Berlin Heidelberg, Biopolymers from Renewable Resources 1998; Chapter 4.
2. Yui, T.; Imada, K.; Okuyama, K.; Obata, Y.; Suzuki, K.; Ogawa, K. *Macromolecules* 1994, 27, 7601.
3. Chi, H.; Houbin, L.; Wuhui, L.; Huaiyu, Z. *Colloid Surf A* 2007, 297, 147.
4. Bernard, B.; Heidenau *Wochenblatt fuer Papierfabrikation* 2005, 133, 1159.
5. Kumar, M.; Ravi, N. V. *React Funct Polym* 2000, 46, 1.
6. Belosinschi, D.; Bobu, E. *Environ Eng Manage J* 2008, 7, 269.
7. Kurita, K.; Koyama, Y.; Nishimara, S.; Kamiya, M.; *Chem Lett* 1989, 1597.
8. Li, J.; Du, Y. M. 230th ACS National Meeting, Washington, DC, Aug. 28–Sept. 1, 2005.
9. Qin, C. Q.; Du, Y. M.; Xiao L. *Polym Degrad Stab* 2002, 76, 211.
10. Rojas, O. J.; Neuman, R. D. *Colloid Surf A* 1999, 155, 419.
11. Li, H. B.; Du, Y. M.; Xu, Y. M.; Zhan, H. Y.; Kennedy, J. F. *Carbohydr Polym* 2004, 58, 205.
12. Steeg, V. D.; Henrica, G. M.; Keizer, A.; Stuart, M. A. C.; Bijsterbosch, B. H. *Nord Pulp Pap Res J* 1993, 1, 34.
13. Ashmore, M.; Hearn, J.; Karpowicz, F. *Langmuir* 2001, 17, 1069.
14. Steeg, V.; Henrica G. M.; Cohen Stuart M. A.; De Keizer A.; Bijsterbosch B. H. *Langmuir* 1992, 10, 2538.
15. Wang, T. K.; Audebert, R. *J Colloid Interface Sci* 1988, 121, 32.
16. Durand, G.; Lafuma, F.; Audebert, R. *Prog Colloid Polym Sci* 1988, 76, 278.
17. Shareef, M.; Ahmed, H. O.; Proceedings of the International Conference on Maritime and Naval Science and Engineering (MN '09), 2nd, Brasov, Romania, September 24–2, 2009; p 129.
18. Vijayakumar, V.; Arivoli, S.; Ramuthai, S. E. *J Chem* 2009, 6, 347.
19. Kennedy, L. J.; Vijaya, J.; Sekaran, G.; Kayalvizhi, K. E. *J Hazard Mater* 2007, 149, 134.
20. Ramuthai, S.; Nandhakumar, V.; Thiruchelvi, M.; Arivoli, S.; Vijayakumar, V. E. *J Chem* 2009, 6, 363.
21. Bobacka, V.; Nösman, J.; Kreutzman, N.; Eklund, D. *Transactions of The 11th Fundamental Research Symposium in Held at Cambridge, September 1997, 1075.*
22. Sarrazin, P.; Beneventi, D.; Chaussy, D.; Vurth, L.; Stephan, O. *Colloid Surf A* 2009, 334, 80.
23. Onabe, F.; Roberts, J. C. *Paper Chemistry*; Blackie: New York 1991; p 198.
24. Miklavic, S. J.; Woodward, C. E.; Jönsson, B.; Aakesson, T. *Macromolecules* 1990, 23, 4149.
25. Sato, T. *J Appl Polym Sci* 1971, 15, 1053.
26. Hedborg, F.; Lindstrom, T. *Nordic Pulp Pap Res J* 1993, 3, 319.
27. Sjöström, E. 1st International Paper Chemistry Symposium Stockholm, Sweden, 1988.
28. Laleg, M.; Pikulik, I. I. *Nord Pulp Pap Res J* 1992, 4, 174.