Available online at www.sciencedirect.com

SCIENCE DIRECT®

Carbohydrate Polymers 58 (2004) 205–214

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Interactions of cationized chitosan with components in a chemical pulp suspension

Houbin Li[a], Yumin Du[a,*], Yongmei Xu[a], Huaiyu Zhan[b], John F. Kennedy[c,d]

[a]*Department of Environmental Science, Wuhan University 430072, Wuhan, China*
[b]*State Key Laboratory of Pulp and Paper Engineering, South China University of Technology 510641, Guangzhou, China*
[c]*Birmingham Carbohydrate and Protein Technology Group, School of Chemical Sciences, The University of Birmingham, Birmingham BI5 2TT, UK*
[d]*Chembiotech Laboratories, University of Birmingham Research Park, Vincent Drive, Birmingham BI5 2SQ, UK*

Received 19 June 2003; revised 30 June 2004; accepted 30 June 2004

Abstract

N-(2-hydroxy-3-trimethylammonio)-propyl chitosan chloride, carboxymethyl chitosan and cationic starch were tested as wet-end additives for peroxide bleached reed kraft pulp. The adsorption of these polysaccharide samples and their interactions with the main components of pulp suspensions (cellulosic fiber, fines, dissolved and colloidal carbohydrates) were investigated by spectrophotometric, microelectrophoresis, particle size and retention/drainage methods. The results showed that the adsorption and aggregation behaviors which occur in pulp suspension were not only affected by the surface physicochemical characteristics of the cellulosic substrates but were also strongly affected by the nature (charge density, charge type and molar mass) of the polysaccharide additives. That is, *N*-(2-hydroxy-3-trimethylammonio)-propyl chitosan chloride additives were almost completely adsorbed onto the surfaces of the cellulosic fibers and aggregated the fines at low dosages, corresponding to those used in industrial operation. The optimum polymer concentration was increased with the reducing of the charge density of the quaternary chitosan additives. The adsorption of cationic starch onto the surfaces of cellulosic substrates was weaker than quaternary chitosan and showed higher optimum polymer concentration. The adsorption of carboxymethyl chitosan promoted the stabilization of the fines and colloidal carbohydrates rather than their aggregation. The polyelectrolyte complexes between hemicelluloses and the quaternary chitosans were formed in the adsorption processing, and these complexes then became adsorbed or deposited onto the cellulosic fibers, and this also correlates to the maximum fines retention and drainage. The experimental results also suggested that the dominant interaction between quaternary chitosan additives and cellulosic substrates are of an electrostatic nature and the fine flocculation was a charge patch mechanism.

Keywords: Quaternary chitosan; Wet-end additives; Adsorption; Reed pulp; Dissolved and colloidal substances; Zeta potential; Retention

---

1. Introduction

In order to improve the physicomechanical characteristic of paper and papermaking process as well as other properties of the end-product (paper), a number of water-soluble polymeric materials have been used. These materials include synthetic polymers (e.g. polyamides, polyacrylamides, polyethyleneimines, etc.) and natural polymers (e.g. starch, cellulose, hemicellulose, guar gum, locust gum, etc.) (Lima, Oliveira, & Buckeridge, 2003; Shen, 1999). Each of these is able to bond with cellulosic substrates by electrostatic or non-electrostatic interaction, which results in improvement of products (paper) properties. Synthetic polymers possess many good properties, but most of them are neither biodegradable nor environmentally clean. Thus natural polysaccharides should be promising additives in the papermaking operation.

Chitosan, a biodegradable, nontoxic, antibacterial, as well as renewable resource, commodity, is the second most widespread natural polysaccharide and is composed of poly[(1→4)-2-acetamido-2-deoxy-β-(D-glucopyranose] and [β-(1→4)-2-amino-2 deoxy-β-D-glucopyranose] (Yan, 1998; Zhao, 2001). Its structure is therefore very similar

---

* Corresponding author. Tel./fax: +86-27-8768-6402.
E-mail address: duyumin@whu.edu.cn (Y. Du).

0144-8617/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2004.06.044

to that of cellulose and it is easily absorbed onto the cellulosic surfaces owing to steric factors and chemical affinity. This results in the improvement of the physico-mechanical properties of paper (Kumar & Majet, 2000; Laleg & Pikulik Ivan, 1992; Tsigos, Martinou, Kafetzopoulos, & Bouriotis, 2000). In addition, cellulosic pulp gains a negative net charge after been bleached by chemicals, and chitosan after been quaternized turns it into cationic derivatives. Thus quaternary chitosan, just as cationic starch, should interact strongly with cellulosic substrates via the electrostatic interaction, and it is likely that quaternary chitosan is more easily adsorbed on to the fiber surfaces, and aggregates the fines, and takes up the dissolved carbohydrates. All of these are beneficial to the papermaking operation. Therefore, quaternary chitosan may be a potential wet-end functional additive in papermaking. The effects of chitosan on the product (paper) properties and the papermaking process were well documented (Allen, Polverari, Levesque, & Francis, 1999; Hou, Yan, & An, 1992; Laleg & Pikulik Ivan, 1993, 1991; Polverri, Allen, Sithole, Gagnon, & Samuel, 2001). But some of these studies were performed at chitosan concentrations much higher than those encountered in industrial applications (Hou et al.; Mucha & Miskiewicz, 2000), and the fundamental studies concerned with the adsorption phenomena and the interactions between cationized chitosan and cellulosic substrates are still not reported.

In this paper, we prepared four samples of *N*-(2-hydroxy-3-trimethylammonio)-propyl chitosan chloride with different degrees of substitution (DS) or molar mass and one sample of carboxymethyl chitosan, and then investigated the adsorption of them onto the surfaces of various cellulosic substrates (cellulosic fibers, fine particle) and the interactions between quaternary chitosan and dissolved and colloidal substances (e.g. dissolved and colloidal hemicellulose, monomeric glucose) in peroxide bleached reed kraft pulp. For comparison, the adsorption of cationic starch was also evaluated in the same situations. In this way, we could obtain a better understanding of the adsorption, the aggregation and uptake phenomena taking place at concentrations representative of those found in industrial papermaking system.

2. Experimental section

2.1. Materials

2.1.1. Polysaccharide additives

Chitosan: A commercial chitosan (provided by Zhejiang Yuhuan Ocean Biochemistry Co Ltd, Zhejiang, China) was dissolved in aqueous 1% (w/w) acetic acid, and 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 by drying. The degree of deacetylation (DD) was determined to be 92% according to Takanori, Keisuke, and Yoshio (1976).

Table 1
The characteristics of quaternary chitosan samples used in this studies

QCS	Molecular weight ($\times 10^5$)	DS (%)
A	2.8	76
B	2.9	61
C	2.9	31
D[a]	1.2	61

[a] Obtained from sample B by ultrasonic degradation.

Quaternary chitosan (QCS): Chitosan sample reacted with 2,3-epoxypropyl trimethyl ammonium chloride and four products were obtained (Xu, Lu, & Ding, 1997). Table 1 shows the molecular parameters of all quaternary chitosan used. The average molecular weight was determined by means of GPC methods (Qin, Du, & Xiao, 2002). These quaternary ammonium salt samples were dissolved in doubly distilled water at a concentration of 0.2% (w/w) before being used.

Carboxymethyl chitosan: This was prepared by carboxymethylation of chitosan (Muzzarelli, 1988), its average molecular weight was about 3×10^5, DS was 71%.

Cationic starch: A commercial cationic starch (DS = 3%) was thermally gelatinized through boiling for 20 min under constant gentle stirring. The solution was then rapidly (within 5 min) cooled to room temperature.

All stock solutions used in the work were always freshly prepared to avoid any possible degradation.

2.1.2. Cellulosic substrates

Peroxide bleached reed kraft pulp (substrate content of 0.5% w/w) was beaten to 35°SR (Shopper-Riegler beating degree) in a Valley beater and followed by ultrasonic-treated for 30 min. ‘Unwashed Pulp’ was a typical pulp containing fibers, fines and related dissolved and colloidal carbohydrates. The fibers and the fines were separated by 200-mesh screen from the Unwashed Pulp suspension, both of which were collected. ‘Fines Suspensions’, containing fines, dissolved and colloidal substances as well as lipophilic extractives, were used directly without examining the substrates content in the experiments, but the fibers separated were thoroughly washed and screened with doubly distilled water in order to get ‘Washed Pulp’. This washing procedure removed the most loosely bound lipophilic extractives, hemicellulose and lignin. Another fraction of the Unwashed Pulp was alkali-treated using aqueous 10% (w/w) sodium hydroxide for 3 h at 40 °C. After centrifugation, the fibrous sediments were thoroughly washed and screened with doubly distilled water until neutral pH was achieved. This pulp was referred to as ‘Alkali-treated Pulp’. The supernatant was neutralized with acetic acid, and the precipitate was coded to as ‘hemicellulose-I ’. The filtrate was treated with ethanol, and the resulting precipitate was called ‘hemicellulose-II ’ (Sun & Tomkinson, 2002).

Microcrystalline cellulose (16 μm average particle size), purchased from Shanghai Chemical Co., China, was thoroughly washed before being used.

The substrates contents of all fiber pulp suspensions were 5 g/l, whereas Fine Suspension, separated from Unwashed Pulp, was used directly without examining the substrates content. All pulp suspensions were stored in refrigeration (4 °C) before being used.

2.2. Methods

2.2.1. Adsorption experiments

Stock solutions of polysaccharide additives (0.2% w/w) were added to the aqueous cellulosic suspensions ($pH \approx 6.6$). The suspensions were gently stirred overnight (around 20 h) with a magnetic stirrer at room temperature to allow adsorption equilibrium to be attained. In order to minimize the effect of carbohydrate adsorption on the vessel surfaces, the total mass of suspension used in the adsorption experiments was constant. The centrifugation method was employed to collect the supernatant because carbohydrates (polysaccharides additives, hemicellulose, degraded cellulose, and sugar) could be adsorbed by the filtration medium (Nylund, Lagus, & Eckerman, 1994). The samples were therefore centrifuged using a Model LD5-10 at 4500 rpm for 30 min, and the supernatant was pipetted off and analysed.

2.2.2. Adsorbed amount of quaternary chitosan

C.I. Acid Orange 7 (15510) was employed to estimate the residual concentration of quaternary chitosan in the supernatant of aqueous pulp suspensions upon the addition of quaternary chitosan additives after attainment of adsorption equilibrium (Gummow & Roberts, 1985). That is, 1 ml of aqueous C.I. Acid Orange 7 (2×10^{-4} w/w) was mixed with 6 ml of the supernatant. The absorbance of the resulting solution at 484 nm was measured with a Model 1601 UV/vis spectrophotometer (Shimdzu, Japan). The residual concentration of quaternary chitosan in the supernatant of pulp suspension was obtained from a calibration curve based on a known sample. The adsorbed amount (Γ) of quaternary chitosan was obtained as follows:

$$\Gamma = (C_i - C_r) \times V/m \tag{1}$$

Where C_i is the initial concentration of quaternary chitosan, C_r is the residual concentration of quaternary chitosan, V is the volume of pulp dispersion, m is the weight of oven dried pulp.

2.2.3. Total residual carbohydrate concentration

The phenol/sulfuric acid spectrophotometric methods (Van de Steeg, de Keizer, Stuart Martien, & Bijsterbosch, 1993) were employed to determine the total residual carbohydrate concentration in the supernatant of aqueous pulp suspensions upon addition of polysaccharides additives after adsorption equilibrium. That is, 4 ml of the supernatant, 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 color solution at 490 nm was measured with a model 1601 ultraviolet-visible spectrophotometer (Shimdzu, Japan) zeroed by the substitution of pure water for an unknown sample.

2.2.4. Particle size and zeta potential

The size of the particles in Fines Suspensions before and after addition of quaternary chitosan was measured by means of photon correlation spectroscopy (PCS) techniques using a N4 Plus Submicron Particle Size Analyzer (BECKMAN COULTER, USA) at 20° C. To estimate the effect of quaternary chitosan on the charge of the fine particle, the zeta potential values of the fine particles in Fines Suspensions were determined (Ashmore, Hearn, & Karpowicz, 2001) using a Model BDL-B microelectrophoresis apparatus (Detecting Instrument Factory, Shanghai Detecting Technology Institute, China). For both measurements, all suspensions upon addition of quaternary chitosan were gently agitated for 20 min, and then centrifuged at 2000 rpm for 2 min.

2.2.5. Retention of fines and drainage performance

In order to correlate the effect of polysaccharide adsorption with the degree of fines retention and drainage in the pulp suspension upon suppression of mechanical entanglement and filtration effects (commonly present during mat formation in paper manufacture), quaternary chitosan (DS = 61%) and cationic starch (DS = 3%) were added to 1000 ml of an Unwashed Pulp suspension containing 2 g of oven dried pulp; after stirring, the ^{0}SR values were measured with a model ZDJ-100 beating degree tester with a 200-mesh screen (Second Materials Factory of Changchun, China) (Yuan, 1959).

3. Results and discussion

3.1. The adsorbed amount of quaternary chitosan onto the cellulosic substrates

The influences of dosage on the adsorbed amounts of quaternary chitosan onto the surfaces of cellulosic substrates for Unwashed Pulp and Washed Pulp are plotted in Fig. 1. It was shown that the adsorbed amount of quaternary chitosan increased with the increasing of the dosage of quaternary chitosan. The adsorbed amount in Washed Pulp was nearly the same as that in Unwashed Pulp at the same dosage, although Washed Pulp contained only the fibers and was in a minimum of fine cellulosic particles and colloidal carbohydrates that can adsorb a part of additives. Considering the dosage of quaternary chitosan, one can conclude that

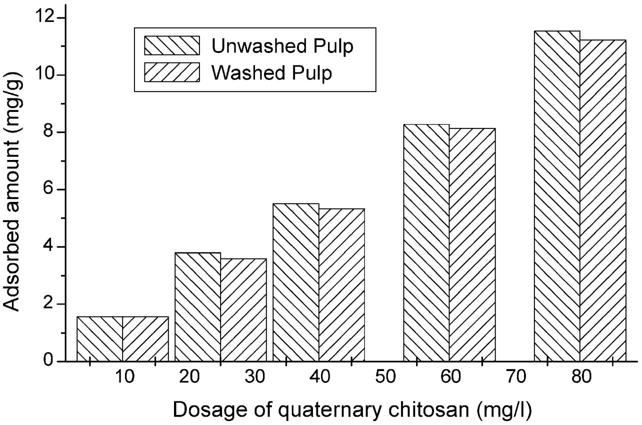

Fig. 1. Adsorption of quaternary chitosan (DS = 31%) on Unwashed Pulp and Washed Pulp (the adsorbed amount was expressed as milligram of quaternary chitosan per gram of oven-dried pulp).

quaternary chitosan was almost completely adsorbed onto the surfaces of cellulosic substrates in the Unwashed Pulp system or Washed Pulp system throughout the concentration range examined.

In the case of Fine suspension, the relationship between the adsorbed amount of quaternary chitosan and the dosage was a curve (Fig. 2). The adsorbed amount increased linearly at first and gradually approached a plateau level as a function of increasing dosage. It seems due to a relatively low amount of the adsorbent (cellulosic substrates). If the dosage was relatively high, free polymer was sufficient to satisfy the increasing adsorption level and was near to the saturation adsorption (plateau level).

3.2. Total residual carbohydrate concentration in the pulp suspensions

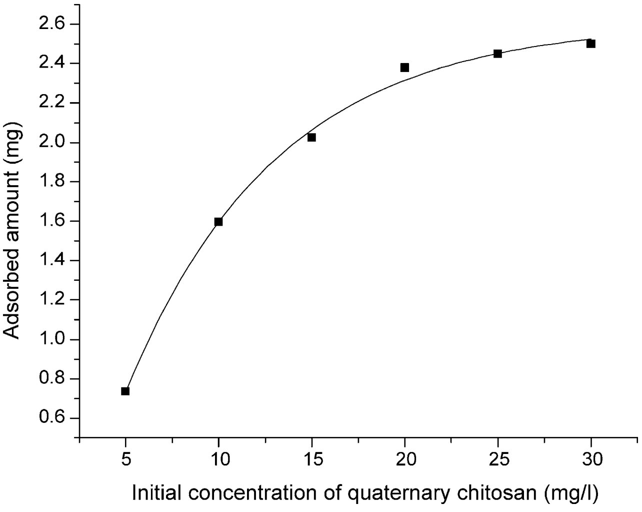

Fig. 2. Adsorption of quaternary chitosan (DS = 31%) for Fine suspension (the adsorbed amount was expressed as milligram of quaternary chitosan per 200 g of Fine suspension).

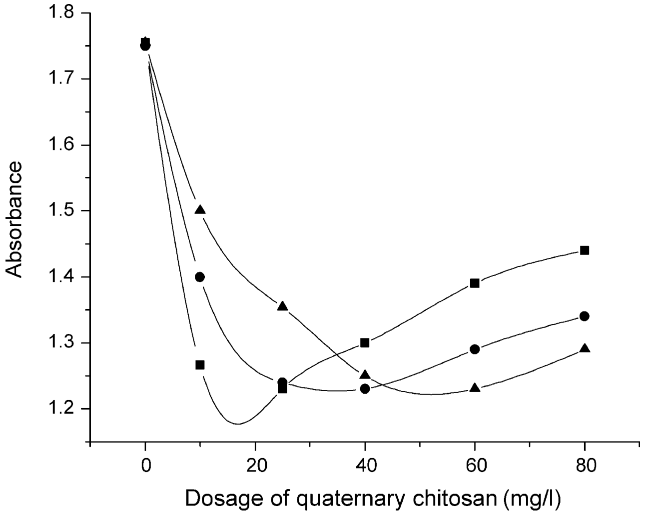

Fig. 3. Absorbance of the supernatant for Unwashed Pulp as a function of initial concentration of quaternary chitosan of different degrees of substitution (■, DS = 76%; ●, DS = 61%; ▲, DS = 31%).

Fig. 3 is the absorbance curves of the supernatant of the Unwashed Pulp suspension upon addition of quaternary chitosan with different degrees of substitution (DS = 31, 61, 76%, respectively). It is clear that the absorbance of the supernatant was reduced and then was in a minimum as the level of quaternary chitosan was increased. As mentioned above, quaternary chitosan was adsorbed not only onto the surfaces of cellulosic fibers but also onto the surfaces of the fine particles and colloidal carbohydrates, and this adsorption resulted in aggregation of fine particles. Thus, the residual carbohydrate concentration of the supernatant was reduced, and the absorbance was decreased. However, the surfaces of cellulosic substrates, especially the surfaces of the fine and colloidal particles, developed a reversal of the sign of the surfaces charge at higher dosage level due to the adsorption of highly charged quaternary chitosan. The fine particles, as will be shown by zeta potential and particle size measurements (Fig. 7), became cationic in character, and were redispersed so that they were not separated from the cellulosic suspension by the centrifugation, and therefore led to be the high absorbance of the supernatant.

It was also shown that the three absorbance curves (Fig. 3) had different critical concentrations. The higher the charge density of quaternary chitosan, the lower the dosage of quaternary chitosan needed to reduce the same amount of carbohydrate in the supernatant. The reason for this behaviour was that the amount of quaternary chitosan, required for charge reversal of the pulp fibers, was low for the high DS, as expected from charge stoichiometric considerations. From these results, it can be concluded that the dominant interactions between quaternary chitosan and cellulosic substrates in the Unwashed Pulp were electrostatic forces. In previous work, authors found that the interactions between chitosan and reed pulp were mainly non-electrostatic forces (e.g. hydrogen bonding) at pH ≈ 6.6 (Li, Du, & Xu, 2004). It seemed to indicate that the charge density of polyelectrolyte additives exert dramatic effects on the model of the interaction between cellulose and chitosan

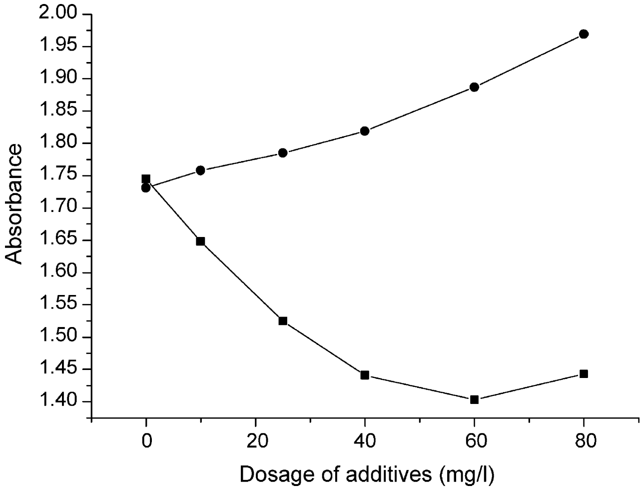

Fig. 4. Absorbance of the supernatant for Unwashed Pulp as a function of initial concentration of cationic starch (■, DS = 3%) and carboxymethyl chitosan (●, DS = 71%).

additives in the system of reed pulp; the higher the charge density, the stronger the electrostatic interactions between the cellulosic substrates and polyelectrolytes. This is consistent with experimental results (Bobacka & Eklund, 1999) and theoretical prediction (Van de Steeg, Stuart Martien, de Keizer, & Bijsterbosch, 1992).

Similar adsorption phenomena took place in the Unwashed Pulp containing cationic starch (Fig. 4), but, for the minimum absorbance of supernatant, both the optimum polymer concentration and the residual concentration of carbohydrates for the system containing cationic starch were higher than those for the system containing quaternary chitosan. The reason for this phenomenon is attributed to the differences originating from the chemical nature. Although, they are both natural polymers of a D-glucose base monosaccharide, chitosan differs from starch. First, the charge density of quaternary chitosan is higher than that of the cationic starch. Second, their molecular configurations are different. The D-glucose units of starch have the α-configurconfiguration and therefore the macromolecule tends to have a helical form (Foster, Whishtler, & Paschall, 1965), whereas chitosan, just as cellulose, is β-linked D-monosaccharide units and tends to have a straight molecular chains (Zhao, 2001). The functional reactive groups of straight polymer molecule are more easily accessible than those of a polymer molecule in a random configuration, and are expected to interact more effectively with the cellulose molecules.

In contrast to the quaternary chitosan and cationic starch, the absorbance of the supernatant of Unwashed Pulp upon addition of carboxymethyl chitosan increased with increasing dosage (Fig. 4). The reason for this phenomenon was that cellulosic fibers, especially cellulosic fine particles and dissolved and colloidal carbohydrates, were likely to be higher negatively charged due to carboxymethyl chitosan adsorption, which was driven by the non-electrostatic forces (e.g. hydrogen binding and Van der Waals forces). In this way, the electrostatic repulsion hindered the aggregation, and at the same time it provided an additional force to disperse the cellulosic fines so that these fines were not separated from the cellulosic suspensions by centrifugation in this condition.

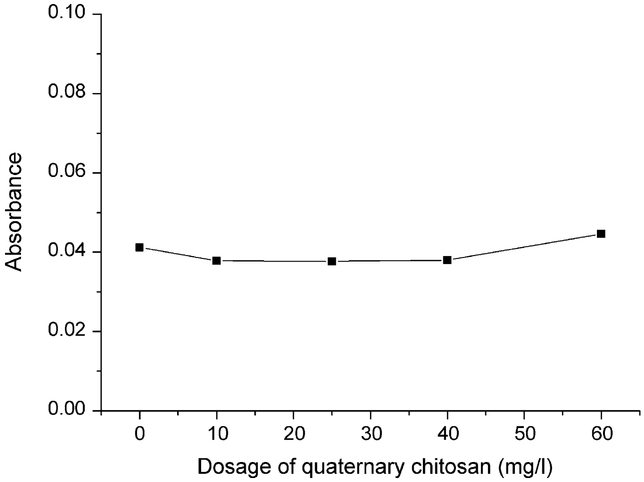

Fig. 5. Absorbance of the supernatant for Washed Pulp as a function of initial concentration of quaternary chitosan (DS = 61%).

The trend of adsorption of quaternary chitosan (DS = 61%) in the Washed Pulp (Fig. 5) indicates that the total residual concentrations of carbohydrates were hardly affected by the dosage of quaternary chitosan at this level. Although, quaternary chitosan became adsorbed onto the surfaces of the cellulosic fibers, fines aggregation and dispersion induced by cationized chitosan did not present in this system due to the minimum of the dissolved and colloidal carbohydrates as well as the cellulosic fines.

The absorbance of the supernatant upon addition of quaternary chitosan with different degrees of substitution and molecular weight in Fines Suspension (Fig. 6) shows

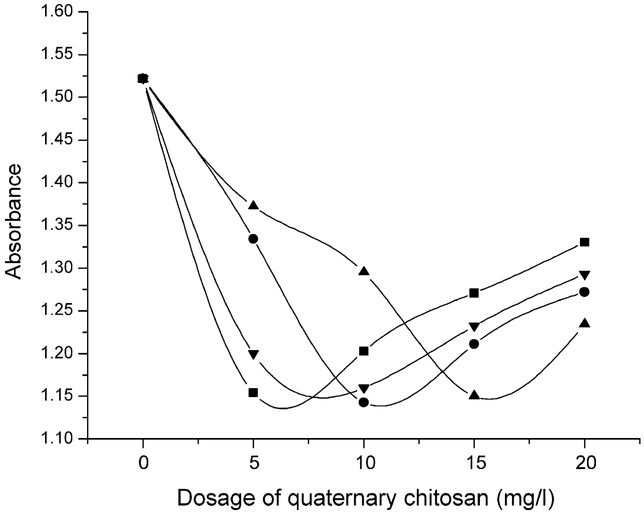

Fig. 6. Absorbance of the supernatant for Fine suspension as a function of initial concentration of quaternary chitosan with different degrees of substitution and molar mass (■, DS = 76%, molar mass is 2.8×10^5; ●, DS = 61%, molar mass is 2.9×10^5; ▲, DS = 31%, molar mass is 2.9×10^5; ▼, DS = 61%, molar mass is 1.2×10^5).

that the total residual concentrations of carbohydrates were reduced and then were in a minimum as quaternary chitosan was increased. This confirmed that cationized chitosan became adsorbed onto the surfaces of the fine particles and colloidal carbohydrates, and flocculated the fine particles. It was also observed that the optimum flocculation concentrations were increased as charge densities of cationized chitosan were reduced (the optimum concentrations for DS = 76, 61 and 31% were about 6, 10 and 15 mg/l, respectively). However, the optimum concentrations were increased with increasing molecular weight (the optimum concentrations for the sample with low-molecular-weight and the sample with high-molecular-weight were about 7 and 10 mg/l, respectively).

3.3. Mean diameter and zeta potential of the fine particles

The change of mean diameter and zeta potential values of the fine particle upon addition of quaternary chitosan (DS = 61%) (Fig. 7) show that the surface charges of the fine particles transformed from negative to zero and then became positive with the increasing of the dosage of quaternary chitosan due to the adsorption. At the same time, the mean diameter of the fine particle increased to a maximum as quaternary chitosan was increased to about 10 mg/l, and then decreased with further increase of the quaternary chitosan level. The observed increase in size was in all cases a consequence of flocculation. When dosage of quaternary chitosan was about 9 mg/l where there was not electrostatic repulsion among the particles, the particles associated easily, thus the mean diameter of the particle was the maximum (the optimal flocculation concentration was at about 10 mg/l of quaternary chitosan concentration). This result was in agreement with the minimum in the residual carbohydrate concentration (around 10 mg/l) of the supernatant of Fines Suspension (Fig. 6). Compared to the concentration (about 9 mg/l) of quaternary chitosan at the isoelectric point with the optimal flocculation concentration (about 10 mg/l), it can be concluded that a charge neutralization mechanism probably play a most important role (Bobacka & Eklund). It confirmed that the interactions between quaternary chitosan and cellulosic substrates were of an electrostatic nature. Due to its high charge density, quaternary chitosan might cause local charge reversal of the surfaces, which resulted in a patch flocculation mechanism (Ashmore et al.,). When the amount of the adsorbed quaternary chitosan was high, the cellulosic particles were positively charged and the flocculation efficiency was decreased, thereby the size of the floc was decreased. When the quaternary chitosan was added in overdose the particle size was approximately the same as that of its anionic precursor. Thus it is likely that the initial adsorption in turbulent conditions was faster (Swerin & Ödberg, 1997) than the patch flocculation process and the adsorbed quaternary chitosan adopt a flatter conformation, which resulted in deteriorated flocculation.

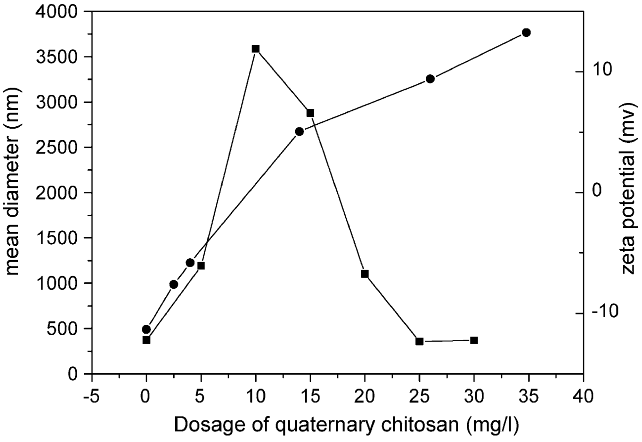

Fig. 7. Comparison of the mean size (■) and Zeta potential (●) of the fines in the filtrate of Unwashed Pulp suspension upon addition of quaternary chitosan (DS = 61%).

3.4. Uptake of carbohydrates and complexation

In order to further understand the interactions of chitosan additives with colloidal and dissolved carbohydrates, which commonly presented in Unwashed Pulp and Fine suspensions, and the effects of the physicochemical characteristics of cellulosic surface on carbohydrate uptake, two cellulose substrates, namely, MCC which is commonly used to simulate cellulosic fines and Alkali-treated Pulp were employed. Hemicellulose-I and hemicellulose-II extracted from Unwashed Pulp suspension (Chen & Wu, 1980) as well as glucose were added to aqueous suspensions of these substrates and equilibrated overnight. The experimental methods were the same as those in the Unwashed Pulp or Fine Suspension except for the added amount of the hemicelluloses and glucose (the hemicelluloses and glucose is 2 and 1% based on oven-dried pulp, respectively). Tables 2–4 show the effects of the quaternary chitosan (DS = 61%) at low dosage level (2 mg of quaternary chitosan per gram of oven-dried pulp) on the absorbance of the supernatant. This absorbance, as was shown earlier, indicated the total residual carbohydrate concentration. It was obvious that the absorbance of the supernatant for the MCC or Alkali-treated Pulp containing hemicelluloses markedly reduced as quaternary chitosan was added

Table 2
The absorbance of the supernatant of MCC and Alkali-treated Pulp suspensions containing hemicellulose-I (H-I) upon addition of quaternary chitosan (DS = 61%)

	Substrate suspension	
	MCC	Alkali-treated Pulp
Quaternary chitosan only	0.038	0.038
H-I only	0.031	0.031
Substrate only	0.062	0.078
Substrate + H-I	0.081	0.082
Substrate + H-I + chitosan	0.62	0.060

Table 3
The absorbance of the supernatant of MCC and Alkali-treated Pulp suspensions containing hemicellulose-II (H-II) upon addition of quaternary chitosan (DS = 61%)

	Substrate suspension	
	MCC	Alkali-treated Pulp
Quaternary chitosan only	0.038	0.038
H-II only	0.041	0.041
Substrate only	0.062	0.078
Substrate + H-II	0.085	0.083
Substrate + H-II + chitosan	0.060	0.064

(Tables 2 and 3). Presumably, either hemicellulose-I or hemicellulose-II formed complexes with polysaccharide additives, and the complexes then became deposited on the substrate surfaces. Such behaviour often occurs in the wet-end of papermaking operations, i.e. the uptake of dissolved carbohydrates. Keen and Opie (1957) also found the same physicochemical phenomenon when they studied the interactions between the pulp suspensions and guar gum. These polyelectrolyte complexes were very effective in modifying surface charges of materials used in paper manufacture (Oertel et al., 1991) and benefit and improve the strength and formation of paper.

However, Table 4 indicated that the absorbance of the supernatant for the system containing glucose was not markedly reduced by the presence of quaternary chitosan. It was concluded that the uptake of glucose by quaternary chitosan additive was negligible, that is, glucose was averse to forming a complex with the quaternary chitosan. This phenomenon was consistent with the experimental result by Sundberg, Ekman, Holmbom, and Harry (1994) who observed that the polyelectrolyte complexes formation between anionic polymers occurring in process waters from peroxide bleached thermomechanical pulp and added cationic chemicals, whereas the formation of these complexes was largely prevented if the anionic polymers were enzymatically degraded to monomers and dimers. Presumably, this phenomenon seemed to be one of the reasons that the absorbance of the supernatant was always greater than zero upon addition of cationic additives (Figs. 2, 3, 5 and 6).

Table 4
The absorbance of the supernatant of MCC and Alkali-treated Pulp suspensions containing glucose (G) upon addition of quaternary chitosan (DS = 61%)

	Substrate suspension	
	MCC	Alkali-treated Pulp
Quaternary chitosan only	0.038	0.038
G only	1.003	1.003
Substrate only	0.062	0.078
Substrate + G	1.050	1.062
Substrate + G + chitosan	1.103	1.102

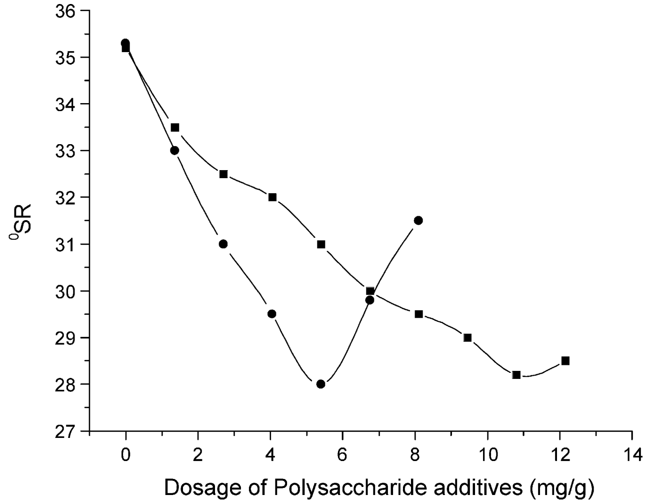

Fig. 8. Retention of fines and drainage for an Unwashed Pulp suspension upon the addition of quaternary chitosan (■, DS = 61%, molar mass = 2.9×10^5) and cationic starch (●, DS = 3%), the dosage is expressed as milligrams of additives per gram oven-dried pulp.

3.5. Retention of fine particles and drainage performance

In industrial operation, the colloidal retention and drainage are very important process parameters, and as such, the ^{0}SR value was measured. In the effect of drainage performance of unwashed pulp suspension upon the addition of quaternary chitosan (DS = 61%) and cationic starch (DS = 3%) (Fig. 8), the ^{0}SR value decreased and then was in a minimum as the polysaccharide additives dosage was increased; this trend corresponded to that of the adsorption experiments (Fig. 3). When polysaccharide additives were added at a low dosage, the following occurred. Firstly, the zeta potential of cellulosic substrates was decreased due to the adsorption of the cationic additives (Fig. 7), and the polarity of cellulosic substrates was reduced, and thus the hydration of the cellulosic substrates was reduced; Secondly, the association or aggregation induced by polysaccharide additives occurred, the BET (Brunauer–Emmett–Teller) surface areas of fine particles, therefore, was decreased. Both of them promoted the dewatering of pulp suspension, and thus ^{0}SR value was decreased. When the dosages were about 5.4 mg of quaternary chitosan per gram of oven-dried pulp and 10.8 mg of cationic starch per gram of oven-dried pulp, respectively, the ^{0}SR values were lowest. This dosage level was in agreement with the minimum residual carbohydrate concentration (ca. 27 mg of quaternary chitosan per liter of unwashed pulp suspension and 55 mg of cationic starch per liter of Unwashed Pulp suspension, respectively) in Unwashed Pulp suspension (see Figs. 3 and 4). Presumably, it also corresponded to the maximum fines-retention concentration. However, at higher dosage of polysaccharide additives, cellulosic fibers, especially fines, as discussed earlier, were overcompensated and became redispersed in pulp suspensions, and so the ^{0}SR value increased and the drainage of pulp suspensions decreased.

Fig. 8 also indicates that quaternary chitosan is more efficient than cationic starch for colloidal retention and drainage properties. This result was consistent with the existence of a residual carbohydrate concentration. As seen in the adsorption experiments, the lowest absorbances were about 1.2 and 1.4 for quaternary chitosan and cationic starch, respectively (see Figs. 3 and 4). These data, which are indicative of the residual carbohydrate concentration of pulp upon the addition of additives, corresponded with the ^{0}SR of pulp suspension, i.e. the lower the residual carbohydrate concentration, the more efficient the retention and drainage performance. The reasons for these, as mentioned above, were likely due to the differences of molecular configuration and molecular parameter (e.g. charge density) between quaternary chitosan and cationic starch. Presumably, quaternary chitosan is more promising wet-end functional additive (e.g. retention aids) than cationic starch.

3.6. Interaction mechanism

It is known that quaternary chitosan is a polyelectrolyte containing hydroxyl groups, cationic groups, and primary amino groups. The bleached pulp substrates contain hydroxyl groups, carboxylic acid groups, and aldehydo groups, and so cellulosic substrates in the reed pulp are thought to be polyanions due to the dissociation of carboxylic acid groups. Therefore, the possible modes of interactions between quaternary chitosan and cellulosic substrates are as follows:

Ionic (electrostatic) interaction. Added to pulp suspension, cationic groups of quaternary chitosan are attractive to the negatively charged sites presenting on the various components of pulp suspensions.

Hydrogen bonding. Quaternary chitosan segments and the surfaces of cellulosic substrates have suitable hydrogen-bonding sites (hydroxyl group-hydroxyl group and hydroxyl group-amino group), and so it is possible for hydrogen bonding to occur.

Van der Waals forces. These interactions are always present between molecules. As quaternary chitosan molecules are near to substrates molecules, the attractive forces are strong for the colloidal systems.

Covalent bonding. Primary amino groups are known to react with carbonyl groups to form imino bonds which are stable in the presence of water, thereby Schiff bases are likely to form between quaternary chitosan and cellulosic substrates.

These interactions can be important in practice, and sometimes all of them operate simultaneously, but often one of them is dominant. Fig. 3 shows that the optimum polymer concentrations were increased as DS of quaternary chitosan was decreased, despite the similar molecular length. Therefore, it was concluded that the electrostatic attraction between quaternary chitosan and reed cellulosic substrates played a central role. This result is congruent with attraction that occurs between cationic potato starch and microcrystalline cellulose (Van de Steeg et al.,).

In the case of the aggregation mechanism, it is known that two common theories, namely, interparticle bridging and patch flocculation, are often used to interpret the interaction behaviors. Interparticle bridging refers to a situation in which the segments of adsorbed polymer extend into a solution and overcome the thickness of the electrostatic double layer of the particle. The adsorbed long-chain polymers extend to the surface of the other particles, thus bridge or bind the particles together and induce association or aggregation, despite the electrostatic repulsion. This interparticle bridging can be achieved with uncharged or charged polymers.

Patch flocculation refers to local charge reversal of the particle surface with an adsorbed oppositely charged polymer. The sites with charge reversal are called patches. 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. For patch flocculation to take place, polymers are often polyelectrolytic with high charge densities and medial molar masses, and there is often a maximum aggregation in the region around the isoelectric point (Shen).

For the fines aggregation induced by quaternary chitosan, the isoelectric point (ca. 9 mg/l) was near to the optimum flocculation concentration (ca. 10 mg/l) in which there was a maximum aggregation (Figs. 6 and 7). This indicated the charge patch flocculation occurred in this system. In addition, the adsorption of low-molar-mass (1.2×10^5) sample resulted in more efficient flocculation than that of high-molar-mass (2.9×10^5) sample (Fig. 6). Due to its high charge density, quaternary chitosan caused local reversal of the fine surface. Thereby there was a charge patch mechanism in the reed pulp. As the amount of quaternary chitosan was same, the low-molar-mass sample contained many more molecules than the high-molar-mass sample, and the patchy sites, formed on the reed fine surfaces, for low-molar-mass sample were also much more than those for high-molar-mass. In this case, the interactions between positively charged patch and negatively charged surface were stronger and the flocculation of reed fines was easier to occur. On the other hand, if the mechanism was bridging binding, the flocculation induced by polymer with high-molar-mass should be much more pronounced than that by high-molar-mass when dosages of flocculants were same. It confirmed that the flocculation mechanism was operated by a charge patch in this system. This was in agreement with theoretical predictions by Böhmer, Evers and Scheutjens (1990), who shown that bridging interaction increased at a low polyelectrolyte adsorption. It was also consistent with a Monte Carlo simulation (Miklavic, Woodward, Jönsson, & Åkesson, 1990) that shown the charge patch was important when the surface was strongly overcompensated by the adsorbed polyelectrolytes.

4. Conclusions

On the basis of these results, it was concluded that both quaternary chitosan and cationic starch, as wet-end additives in papermaking, were adsorbed onto the surfaces of the cellulosic substrates (cellulosic fibers, cellulosic fines, colloidal carbohydrates) of bleached reed kraft pulp at very low dosages representative of those found in industrial practice. Whereas the adsorption of quaternary chitosan was more effective than that of cationic starch due to the differences in the molecular configuration and the charge densities. Carboxymethyl chitosan with negative charge was also adsorbed and thus resulted in the stabilization of the fines and colloidal carbohydrates. These adsorption and aggregation behaviors were affected not only by the surface physicochemical properties of cellulosic substrates but also by the nature (e.g. charge characteristic, degree of substitution, molecular configuration and molecular weight) of polyelectrolyte additives. The dominant interactions between cellulosic substrates and additives were charge neutralization. That is, the higher the charge density of quaternary chitosan, the lower would be the optimum polymer concentration. It was also observed that there were the polycation–polyanion complexes between quaternary chitosan and dissolved hemicelluloses, whereas glucose was averse to forming a complex with the quaternary chitosan. The polyelectrolyte complexes were then retained on the cellulosic fibers, i.e. the uptake of soluble hemicellulose by quaternary chitosan obviously took place in the adsorption process.

Acknowledgements

We are grateful for the financial support of this research from National Natural Science Foundation of China (Grant No. 29977014). We also thank Xianqin Qiu for the providing Valley beater and ^{0}SR tester.

References

Allen, L., Polverari, M., Levesque, B., & Francis, W. (1999). Effect of system closure on retention and drainage aid performance in TMP newsprint manufacture. *Tappi Journal*, *82*(4), 188–195.

Ashmore, M., Hearn, J., & Karpowicz, F. (2001). Flocculation of latex particles of varying surfaces charge densities by chitosan. *Langmuir*, *17*, 1069–1073.

Bobacka, V., & Eklund, D. (1999). The influence of charge density of cationic starch on dissolved and colloidal material from peroxide bleached thermomechanical pulp. *Colloids and Surfaces, A: Physicochemical and Engineering Aspects*, *152*, 285–291.

Böhmer, M. R., Evers, O. A., & Scheutjens, J. M. H. M. (1990). Weak polyelectrolytes two surfaces: adsorption and stabilization. *Macromolecules*, *23*, 2288–2301.

Chen, G. F., & Wu, Y. M. (1980). *Plant fiber chemistry* (p. 223). Beijing, China: Light Industry Press.

Foster, J. F. (1965). In R. L. Whishtler, & E. F. Paschall, *Starch: Chemistry and Technology* (1) (pp. 349–392). New York: Academic Press.

Gummow, B. D., & Roberts, G. A. F. (1985). Studies on chitosan-induced metachromasy, 1: metachromatic behavior of sodium 2-hydroxy-1, 1′-azonaphthalence-4-sulfonate in the presence of chitosan. *Macromolecular Chemistry*, *186*, 1239–1244.

Hou, S. Z., Yan, Z., & An, Y. Q. (1992). Effect of chitosan-starch phosphates on paper strength and filler retention. *China Paper and Pulp*, *11*(6), 27–32.

Keen, J. L., & Opie, J. W. (1957). Colorimetric method as a means of studying carbohydrate sorption on pulp. *Tappi Journal*, *40*, 100–104.

Kumar, R., & Majet, N. V. (2000). A review of chitin and chitosan application. *Reactive and Functional Polymers*, *46*(1), 1–27.

Laleg, M., & Pikulik Ivan, I. (1991). Wet-web strength increase by chitosan. *Nordic Pulp and Paper Research Journal*, *6*(3), 99–103 (see also page 109).

Laleg, M., & Pikulik Ivan, I. (1992). Strengthening of mechanical pulp webs by chitosan. *Nordic Pulp and Paper Research Journal*, *7*(4), 174–180.

Laleg, M., & Pikulik Ivan, I. (1993). Unconventional strength additives. *Nordic Pulp and Paper Research Journal*, *8*(1), 41–47.

Li, H. B., Du, Y. M., & Xu, Y. M. (2004). Adsorption and complexation of chitosan wet-end additives in papermaking systems. *Journal of Applied Polymer Science*, *91*(4), 2642–2648.

Lima, D. U., Oliviera, R. C., & Buckeridge, M. S. (2003). Seed storage hemicellulose as wet-end additives in papermaking. *Carbohydrate Polymers*, *52*, 367–373.

Miklavic, S. J., Woodward, C. E., Jönsson, B., & Åkesson, T. (1990). Interaction of charge surfaces with grafted polyelectrolytes: a Poisson–Bolzmann and Monte Carlo study. *Macromolecules*, *23*, 4149–4157.

Mucha, D. M., & Miskiewicz, D. (2000). Chitosan blends as filler for paper. *Journal of Applied Polymer Science*, *77*, 3210–3215.

Muzzarelli, R. A. A. (1988). Carboxymethylated chitin and chitosan. *Carbohydrate Polymers*, *8*, 1–21.

Nylund, J., Lagus, O., & Eckerman, C. (1994). Character and stability of colloidal substances in a mechanical pulp suspension. *Colloids and Surfaces, A: Physicochemical and Engineering Aspects*, *85*, 81–87.

Oertel, U., Petzold, G., Buchhammer, H., Geyer, S., Schwarz, S., Muller, U., & Ratzsch, M. (1991). Interaction of surface charge into polymers by polyelectrolyte complexes. *Colloids Surfaces*, *57*, 375–381.

Polverri, M., Allen, L. H., Sithole, B., Gagnon, P., & Samuel, J. F. (2001). The effect of coverting from 100% OCC to 50% OCC 50% NSSC on retention and drainage in a closed-cycle paperboard mill. *Tappi Journal*, *84*(1), 99.

Qin, C. Q., Du, Y. M., & Xiao, L. (2002). Effect of hydrogen peroxide treatment on the molecular weight and structure of chitosan. *Polymer Degradation and Stability*, *76*, 211–218.

Shen, Y. D. (1999). *Preparation and Mechanism of Paper Chemicals*. Bejing, China: Light Industry Press (Chapter 3).

Sun, R. C., & Tomkinson, J. (2002). Characterization of hemicelluloses obtained by classical and ultrasonically assisted extractions from wheat straw. *Carbohydrate Polymers*, *50*, 263–271.

Sundberg, A., Ekman, R., Holmbom, B., & Harry, G. (1994). Interactions of cationic polymers with components in the thermomechanical pulp suspensions. *Paper Puu*, *76*(9), 593–598.

Swerin, A., & Ödberg, L. (1997). *Transactions of the 11th Fundamental Research Symposium, Cambridge, September 1997* (II) (p. 265). UK: Pira International.

Takanori, S., Keisuke, K., & Yoshio, I. (1976). Studies on chitin, 2 Effect of deacetylation solubility. *Macromolecular Chemistry*, *177*, 3589–3600.

Tsigos, I., Martinou, A., Kafetzopoulos, D., & Bouriotis, V. (2000). Chitin deaectylases: new, versatile tools in biotechnology. *Trends in Biotechnology*, *18*, 305–311.

Van de Steeg, H. G. M., Stuart Martien, A. C., de Keizer, A., & Bijsterbosch, B. H. (1992). Polyelectrolyte adsorption: a subtle balance of forces. *Langmuir*, *10*, 2538–2546.

Van de Steeg, H., de Keizer, A., Stuart Martien, A. C., & Bijsterbosch, B. H. (1993). Adsorption of cationic starches on microcrystalline cellulose. *Nordic Pulp and Paper Research Journal*, *8*(1), 34–40.

Xu, Z., Lu, C. H., & Ding, M. T. (1997). Preparation and characterization of quaternary chitosan. *Journal Functional Polymer*, *1*, 51–55.

Yan, R. X. (1998). *Water-soluble polymer*. Beijing, China: Chemical Industry Press (Chapter 11).

Yuan, Z. (1959). *Paper and pulp analysis* (p. 247). Shanghai, China: Shanghai Science and Technology Press.

Zhao, T. D. (2001). *Chitosan*. Beijing, China: Chemical Industry Press (Chapter 1).