Flocculation of Reed Pulp Suspensions by Quaternary Chitosan-Nanoparticle SiO$_2$ Retention Aid Systems

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ABSTRACT: The microparticle retention aid system has been a focus on the studies of paper-making chemicals. *N*-(2-Hydroxy-3-trimethylammonio)-propyl chitosan chlorider [quaternary chitosan (QCS)]—nanoparticle SiO$_2$ dual component system was investigated in this work. The adsorpton kinetic experiments indicated that there was a very fast (<1 min) polymer adsorption under good mixing conditions. Adsorption of QCS onto the fiber surface was followed by a rearrangement to reach an equilibrium conformation. At the same time, QCS chains, existing on the surface of fiber, could permeate into the porous of the fiber, resulting in the reducing of zeta potential of the cellulosic fiber. In addition, the flocculation would be increased with the increasing of SiO$_2$ when the fiber substrates surfaces was net positively charged by an adsorbed QCS layer. It was also found that ionic strength decreased significantly the flocculation efficiency in pure QCS system, whereas the turbidity of the reed pulp suspension increased slightly with the increasing of NaCl concentration in QCS-SiO$_2$ systems. The effect of shear force on the flocculation was tested. It was shown shear led to floc breakage and decreased the flocculation. These phenomena were very obvious for one-component system (QCS or C-St), but the microparticle system (QCS-SiO$_2$ or C-St-SiO$_2$) was shear resistance. Dynamic drainage experiment indicated that the turbidity of white water was decreased with the increasing of dosage of SiO$_2$ in experimental level. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 742–749, 2010

Key words: quaternary chitosan; microparticle retention; flocculation; wet-end additives

INTRODUCTION

To meet the demand for higher production efficiency in paper making, two kinds of flocculant systems had been used. One of them was the single-component system such as cationic polyacrylamide,[1] cationic starch,[2] and quaternary chitosan (QCS).[3] The other was the dual-component retention aid system consisting of two polyelectrolytes, which were added in sequence and gave synerigistic effects with regard to the retention of fine material in wet end of the paper machine.[4] It was known that the flocculation performance was high for the single-component system, but the retention efficiency was sensitive to the ionic strength of the paper-making media, and the flocs formed in this system were tend to be broken in turbulent flow, which resulted in the decreasing of retention of fines or fillers.[5] For dual component, it exhibited better shear resistance compared with single-component polyelectrolyte system, the flocs disruption was not to occur as easily as

that in single-component system when subjected to shearing.[6] This phenomenon was important for a modern high speed paper machine.[7]

In recent years, a new kind of dual component retention aid system had become more available to the paper maker. These systems were named microparticle systems and the different systems, such as Hydrocol,[8] Hydrsil, and Compozil,[9] showed some common features that distinguish them from the conventional dual polymer retention aid systems: reflocculation took place after flocs breakage if a microparticle system was being used[10]; A positive dewatering effect was often seen both in the wire section and in the press section[11]; The dried sheet often showed a higher permeability when a microparticle system was being used.[12]

In this article, a novel microparticle retention system consisting of QCS and anionic silica was explored. The effects of hydrodynamic shear force, electrolyte concentration, and flocculate time on the flocculation of reed kraft pulp suspension were investigated. For comparison, the flocculation by cationic starch-nanoparticle SiO$_2$ system was also evaluated in the same situations. In this way, we can have a better understanding of the retention- and

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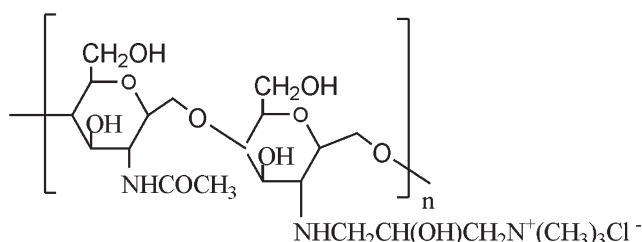
Figure 1 The structure of quaternary chitosan.

drainage-aid performance of microparticle system for the cellulosic fines and fillers in industrial paper-making operation.

EXPERIMENTAL SECTION

Materials

Cellulosic substrates

Bleached reed kraft pulp was beaten to 38.5°SR (30°C) in a PFI beater (100 – 1PFI, Hongkong Yongxian Electron instruments Ltd.) to increase the specific surface area of the fibers before the addition of additives. The weighted average length of cellulosic fibers were 0.87 mm and 0.81 mm within 0.2–7.2 mm and 0–7.2 mm, respectively. The number average length of cellulosic fibers were 0.55 and 0.39 mm within 0.2– 7.2 mm and 0 –7.2 mm, respectively.

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

Quaternary chitosan

QCS (Fig. 1) were prepared using a nucleophilic substitution reaction in our laboratories 13, this is, a commercial chitosan (provided by Zhejiang Yuhuan Ocean Biochemistry, Zhejiang, China) reacted with 2,3-epoxypropyl trimethyl ammonium chloride and two products were obtained. Table I listed the molecular parameters of QCSs used. The average molecular weight was determined by means of GPC methods.[13] These quaternary ammonium salt samples were dissolved in distilled water at a concentration of 0.2% (w/w) before being used.

Cationic starch (C-St): A commercial potato starch (DS = 0. 03, M_w = 40 × 106, bought from Guangxi Mingyang Starch Factory) with quaternary ammonium substituent and chloride as counter ion 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.

Anionic silica (friendly presented by Prof Dan) with a surface area of 385 m^2/g and an average particle size of 13 nm was used in the experiments. The colloidal solution was prepared by this anionic silica with the concentration of 0.01% (w/w) by distilled water, and was treated for 30 min by ultrasonic (SCQ-3201A, 250W, 30KHZ, Shanghai Shenyan Ultrasound machines) before using.

$CaCO_3$ used in this study was a commercial available chalk from Qingxing chemical (Taiwan, China). The specific surface area of this material is 1.47 m^2/g, the mean particle size is 2.69 μm, 42% by weight consists of particles less than 2 μm in diameter. The chalk contains about 98.4% $CaCO_3$ and 1.6% impurities. The noncarbonic matter consists of SiO_2 (0.2%), MgO (0.16%), and Fe_2O_3 (0.02%). All numbers were given by the manufacture. The charge characteristic of the calcium carbonate was obtained from electro kinetic measurements in $0.001M$ NaCl solution showing a value around −43.9 mV at pH = 8.

Methods

Flocculation studies

Bleached reed kraft pulp (38.5°SR) was refined for 5 min and was diluted to 0.2% (w/w) with deionized water. The resulting cellulosic pulp was added by NaCl solution until NaCl concentration was 0.005 mol/L. After stirring, QCS or cationic starch was added. When the dispersion was stirred for 30 s, silica solution was added, and then the mixing solution was treated on AQUA LYTIC (Germany) flocculator under the controlled time and shear stress. After flocculation, the dispersion was sedimented for 5 min and the residual turbidity of the supper solution was measured at turbidity tester.

The zeta potential of the fiber surfaces and potentiodynamic measurement

The refined pulp with a solid content of 0.2% (w/w) was dispersed in 0.005 mol/L NaCl solution, and then QCS was added to the pulp suspension. After stirred for 30 s, the zeta potential values of the fiber in suspensions were determined using a Model BDL–B microelectrophoresis apparatus (Mütek SZP06, Germany) at 20°C. For potentiodynamic measurement, the experimental method was similar to the zeta potential method above, but the zeta potential was recorded in interval time.

Dynamic drainage

The dynamic drainage jar (DDJ) is a common and reliable tool to evaluate retention and drainage of

TABLE I
The Characteristics of Polysaccharide Additives Used in this Studies

	Molecular weight (×10^5)	Degree of substitution (%)
QCS93	19.0	93
QCS69	17.5	69
C-St	400	3
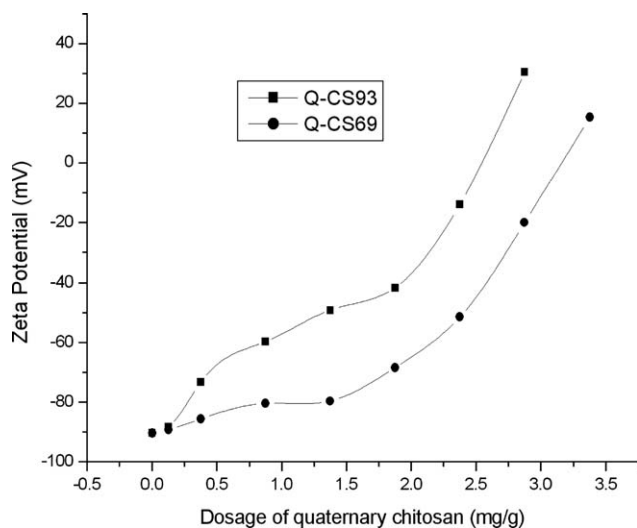
Figure 2 The effects of quaternary chitosan on the zeta potential of fibers.

single- or multicomponent flocculation systems under conditions that are quite similar to large-scale paper-making processes. In the present work, a DDJ with a 300-mesh bottom screen and an impeller speed of 400 or 900 rpm was used.

RESULTS AND DISCUSSION

### ξ-Potential of the fiber and adsorption dynamics of QCS

QCS, as a polyelectrolyte, was adsorbed by cellulosic substrates via electrostatic forces. This adsorption of a polyelectrolyte to an oppositely charged surface could be seen as an entropy-driven ion-exchange process where counter ions bound to the surface were replaced by the large macro-ions.[14] As a result of the adsorption, the ξ-potential values of cellulosic fibers were changed. Figure 2 showed the effects of QCS on the ξ-potential of fibers. With the increasing of QCS, the ξ-potential of fibers gradually transfer from negative to zero and then to positive due to the adsorption of QCS. But QCS93 had a more remarked shifting tendency. As ξ-potential of fibers was 0 V, the dosages of QCS93 and QCS69 were in about 2.5 mg/g fiber and 3.1 mg/g fiber, respectively. This was because that the electro-neutralization of polyelectrolyte was strongly charge densities dependent, and the charge density of QCS93 was higher than QCS69. When ξ-potential of reed fibers were zero, the corresponding surface excess value for the QCS93 was lower than that for QCS69.

It was known that the adsorptive configuration of polyelectrolyte was very important for the flocculation and retention of the cellulosic substrate, and the conformation properties of the polyelectrolyte at solid surfaces changed with the adsorptive time. To

better understand the flocculation by QCS, ξ-potential of the fibers were measured as a function of time after the addition of polyelectrolyte solution into reed suspension. Figure 3 depicted the effect of the contact time on the ξ-potential of reed fiber upon the addition of QCS93 (4.4 mg/g of dosage) in a 0.005 mol/L NaCl solution. It was found that ξ-potential of reed fibers was ca. +5.5 mV at initial adsorption of QCS93. With the increasing of the adsorptive time, a rapid fail and then a plateau in ξ-potential ($\xi \approx -1.6$ V) were observed.

One explanation of this phenomenon could be a reformation of the adsorbed polyelectrolyte. When QCS was added into the reed fiber dispersion, the adsorption occurred at once. At this time, a part of QCS segments, which were referred as the trains, were extended on the reed substrates. Whereas the other part of QCS segments, which were referred as the chain loops and the tails, protruded into the aqueous medium. The electrostatic double layer between the diffusion layer and the immobile phase could form. Because of QCS with high positively charge, ξ-potential of the fibers was high (+5.5 mV). However, with the process of the adsorption time, the reformation of adsorbed QCS could take place, that is, the chain loops and the tail fractions gradually changed into the trains. This reformation made the electrostatic double layer to collapse, so the ξ-potential was fallen to 0 V at the adsorption time of about 600 s as shown in Figure 3.

Another explanation of the fail in ξ-potential was likely the permeation of QCS chains into the porous of the fiber. In general, there were a great number of micropores with a diameter of 5–10 nm in the surfaces of the reed fibers.[15] QCS molecule permeated into the porous fibers, and ξ-potential was fallen to zero even to negatively value.[16]
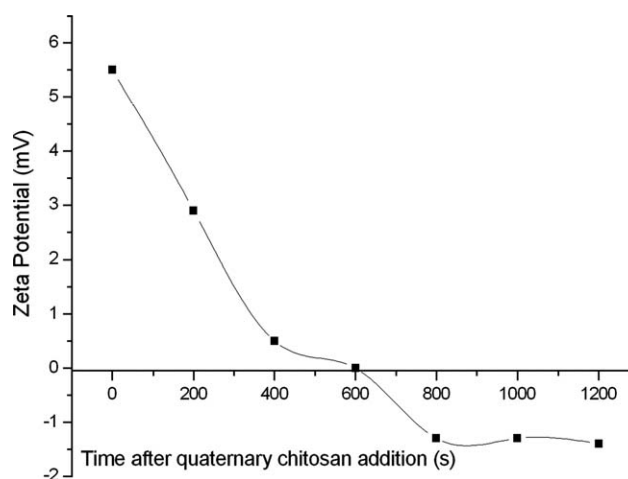
Figure 3 The effects of the time after quaternary chitosan addition on the zeta potential of fibers.
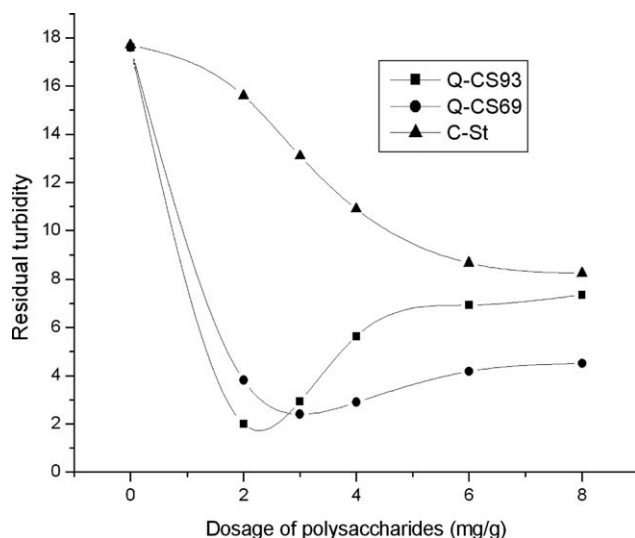
Figure 4 Flocculation induced by single-component system.

The flocculation of reed pulp

The flocculation by single-component system

Figure 4 presented the residual turbidity curves of reed pulp on the addition of single-component system (QCS93, QCS69, or cationic starch). For QCS93 and QCS69 system, the curves showed the similar trends: the residual turbidity of reed pulp was reduced and then was in a minimum as additives were increased. This was likely because that the fines presented in pulp system were aggregated by polyelectrolyte. On the addition of QCS into reed pulp, the adsorbed QCS declined ξ-potential of reed fine, the electrostatic repulsion between the fines was decreased, and the collision lead the fines to destabilize. In addition, the patch flocculation was occurred when QCS was added.[17] As discussed in our earlier works, the positively charged patches, which were formed on the cellulosic substrate surfaces, attracted the negative patches that represent the original fiber surfaces, and the flocs between the fines were formed. These should result in the decreasing of the residual turbidity of the reed pulp.

However, when the dosage of QCS was high, the cellulosic substrate surfaces were overcompensated, namely, cellulosic substrates gained positive charge. Therefore, the repulsion forces between these positively charged fines could increase the residual turbidity of reed pulp. This phenomenon was consistency to the flocculation of alumina, silica, and zircon suspensions induced by polyelectrolytes chitosan and polyacrylic acid.[18] Figure 5 demonstrated the optimum dosage of 2.4 mg/g for QCS93 and 3 mg/g for QCS69, respectively. These results were in accordance with their isoelectric points. But in the case of cationic starch, the optimum dosage was not

observed within the experimental dosage level. The reason for this was that the addition of cationic starch was too low for the cellulosic substrate surfaces to develop a reversal of the surface charge. The flocculation by cationic starch (7.2 mg/g)-SiO$_2$ system, as shown in Figure 8, confirmed this phenomenon.

### The flocculation by dual-component QCS-SiO$_2$

In this experiment, the addition of QCS93 and QCS69 were 3.2 mg/g and 3.6 mg/g, respectively, this dosage levels were higher than the dosage of the maximum flocculation (Fig. 5). Presumably, the surfaces of cellulosic substrates were overcompensated and were positively charged in these situations.

When the colloidal silica was added to the pulp system pretreated by QCS, the residual turbidity of reed pulp was investigated. Figure 5 showed the effect of silica on the residual turbidity of reed pulp on the addition of QCS at pH = 8. The results demonstrated that the residual turbidity of reed pulp was decreased with the increasing of the dosage of SiO$_2$. The reason for this was as follows: When negatively charged silica was added, QCS-SiO$_2$ complexes were formed. These complexes reduced the interaction between the segments of polyelectrolyte and substrates surfaces. This could lead some trains on the surfaces of the substrates to rearrange in chain loops and tails,[14] and thus the strong bridging flocculation took place in QCS-SiO$_2$ system. This phenomenon indicated that QCS-SiO$_2$ system, as a flocculants system, was expected to be more efficient than QCS system.

Figure 5 also showed that the residual turbidity of reed pulp treated by QCS69-SiO$_2$ system was lower than that by QCS93-SiO$_2$ system. As seen above, the
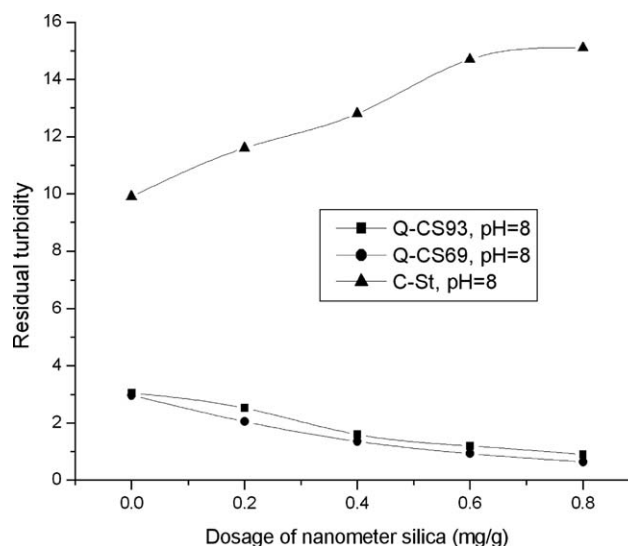
Figure 5 The flocculation efficiency of polyelectrolyte-SiO$_2$ system.
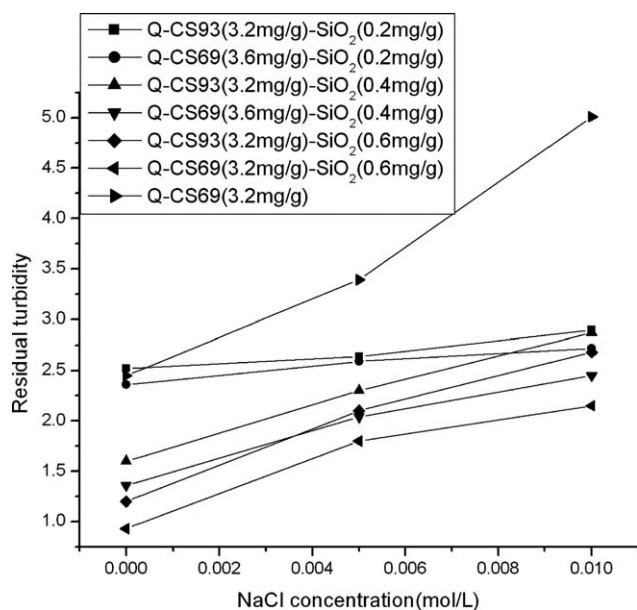
Figure 6 The effects of ionic strength on the flocculation by QCS-SiO$_2$ and QCS.

electrostatic interaction between polyelectrolyte and reed fiber surface was charge density dependent. For the polyelectrolyte with low-charge density, there were relatively more chain loops and tails, which stretched into the aqueous medium. However, QCS with high charge density was adsorbed in more extended conformation, polymer chain was in more trains form on the substrates surfaces, and thus the bridging flocculation was fallen. This result was in agreement with the microparticulate retention aid system consisting of cationic polyacrylamide and anionic montmorillonite,[19] and was confirmed by Sennerfors et al.,[14] who claimed that it was a 7-fold increase in layer thickness in the presence of nano-particles for the system with the low-charged CPAM, and a 5-fold increase in thickness in the system consisting of high charged CPAM-SiO$_2$.

However, there was a increasing of the residual turbidity of pulp suspension in the cationic starch-SiO$_2$ system. This was likely that cellulosic substrates were still net negatively charged at 3.2 mg/g of cationic starch addition. Therefore, the electrostatic repulsion should lead the dispersed fines to more stable as negatively charged SiO$_2$ was added, and the residual turbidity of reed pulp was increased with the increasing of SiO$_2$. This phenomenon also confirmed the results that the silica gave a flocculating effect only after passing the flocculation maximum in microparticle retention aid system.[19]

The effect of electrolyte concentration on the flocculation

The electrolyte concentration can affect the performance of a retention aid system. Flocculants that

depend on electrostatic interactions are naturally sensitive to the ionic strength. These aspects are becoming more important due to the increasing system closure in paper mills.

Figure 6 showed the effect of electrolyte (NaCl) concentration on the residual turbidity of the reed pulp on the addition of singe-component (QCS69) or dual-component systems (QCS69-SiO$_2$). It was observed that ionic strength was significantly decreased the flocculation efficiency in pure QCS69 system, whereas the turbidity of the reed pulp suspension was slightly increased with the increasing of NaCl concentration in QCS-SiO$_2$ systems. Theoretical discussion of how ionic strength affected the conformation of polyelectrolyte was available in the literature.[20] NaCl could screen not only the segment–segment repulsion of QCS but also the attractions of QCS segment with the surfaces such as cellulosic negatively charged surface as well as SiO$_2$ particle surfaces.

For the pure QCS69 system, the screening of polyelectrolyte-fiber surface reduced the adsorption when NaCl was added, the decreasing of the repulsive forces between QCS segments lead QCS chain loops and tails to become more compact statue, QCS adsorptive layer therefore was much thin, the bridging flocculation was obviously decreased, and thus the residual turbidity of the reed pulp was greatly increased at high NaCl concentration conditions.

In the case of QCS-SiO$_2$ systems, the flocculation was maintained up to a higher NaCl concentration. It was likely that polyelectrolyte-silica complexes decreased the electrostatic interactions which presented in QCS loops and tails, the screening was weakness, i.e., QCS-SiO$_2$ system was not sensitive for the added electrolyte concentration due to the low-charged density. This phenomenon was similar to the description in Ref. [20] that nonionic PAM-montmorillonite system seemed to be only slightly affected by NaCl.[21]

The effect of shear force on the flocculation

It was know that high speed of paper machine was a tendency for the paper making. The higher production efficiency should lead to more turbulent flow conditions. Although the turbulent status of fiber pulp suspension was critical for the retention of the fines and the fillers, and as such, the flocculation by single-component system (QCS93, cationic starch) and dual-component system (QCS93-SiO$_2$, cationic starch-SiO$_2$) was studied. The shear level was changed by increasing the pump speed. Figure 7 showed the residual turbidity of reed pulp suspension at different Reynolds number as the contact time between reed pulp suspension and additives was about 3 min. For the QCS93 (3.2 mg/g) and
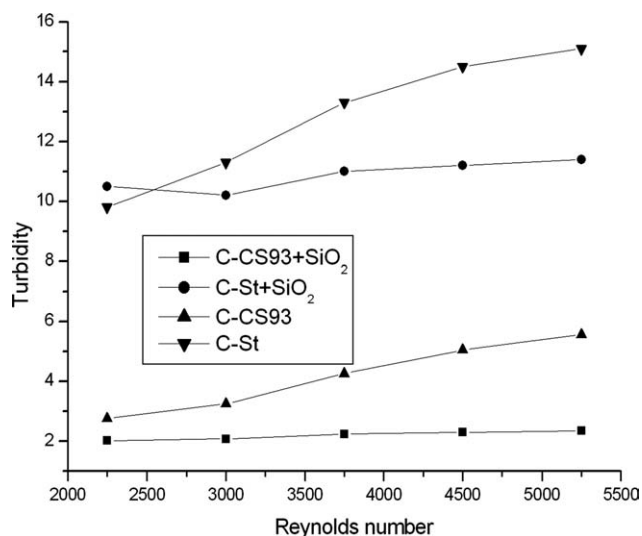
Figure 7 The effects of shear on the flocculation by additives.

cationic starch (7.2 mg/g), the residual turbidity was increased with the increasing of Reynolds number, whereas the residual turbidity was almost the same for the different shear level when the QCS93 (3.2 mg/g)-SiO_2 (0.4 mg/g) or cationic starch (7.2 mg/g)-SiO_2 (0.4 mg/g) system was used.

From submicroscopic aspect, the interaction forces between polyelectrolyte and cellulosic substrates in two-component system were not as strong as in the one-component system, but there were long-ranged forces in the polyelectrolyte and SiO_2. These long forces were dependent on the turbulent flow conditions of the pulp system, i.e., it was weak as turbulence of pulp system was severe, whereas it could be reformed as the shear was decreased.

When a higher shear was applied, the flocs initially formed as a result of QCS addition were broken. The loops and the tail segments of the adsorbed polyelectrolyte, which initially presented on the substrates surfaces, tended to rearrange in a flat configuration because of a degradation of polymer chain by flocs breakage.[14] When shear rate returned low, the bridge flocculation was still difficult due to chain breakage, and the flocculation efficiency was decreased. On the other hand, the long-ranged force between polyelectrolyte and SiO_2 tended to aggregate the breakage flocs, the reflocculation, therefore, could take place when shear stress returned weak. Figure 7 appeared the long-rang attraction dominated the flocculation process in above two antagonistic effects for QCS-SiO_2 system. This result was in agreement with cationic polyacrylamide and anionic montmorillonite system.[22]

However, in the case of single system (QCS), there were only flocs breakage and the reconformation[23] of QCS molecular chain, and were not long-ranged

forces due to the absence of nano-SiO_2. It was obvious that a reduction in the molecular weight of QCS molecules should decrease the bridging capability,[24] and thus the residual turbidity of white water was decreased even if the shear force was changed to a low level.

The effect of contact time on the flocculation

Figure 8 showed the effect of contact time between polyelectrolyte–nano-SiO_2 system and fiber suspension on the flocculation of reed pulp. An almost same residual turbidity was observed for the different flocculation time (1–6 min) in three systems (QCS93-SiO_2, QCS69-SiO_2, cationic starch-SiO_2). This was against to the general results that flocculation occurred in less than 1 s.[25] The reason for this was likely because that the flocculation had reached equilibrium state in 1 min. The present measurements could not be made at very short time (less than 1 s). But this phenomenon demonstrated that from the other side the flocculation by microparticles retention system was rapid. It could be reasonable that the maximum flocculation was almost independent on the contact time in industrial operation.

Dynamic retention performance

To further understand the retention performance of QCS-SiO_2 system in industrial operation, we added $CaCO_3$ filler into reed pulp suspension, and then measured the dynamic retention property of polyelectrolyte–nano-SiO_2 system by a DDJ tester. Figure 9 showed the relationship of turbidity of white water with the dosage of dual-component system. For QCS-SiO_2 system, the turbidity was decreased with
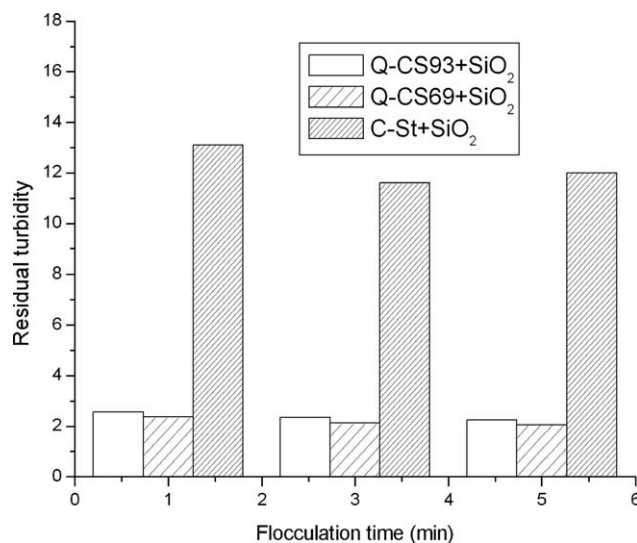
Figure 8 The effects of time on the flocculation by polyelectrolyte-SiO_2 systems.
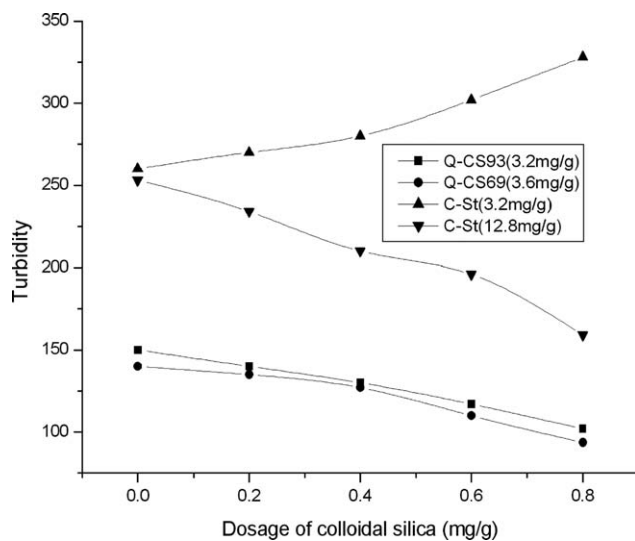
Figure 9 The DDJ retention by polyelectrolyte-SiO$_2$ systems.

the increasing of dosage of SiO$_2$ in the experimental level. Nevertheless, the retention efficiency was relative to the charge density of polyelectrolyte at the same dosage of SiO$_2$. As discussed above, QCS69-SiO$_2$ had more chain loops and tails which exposed in solution, and thus the bridging capability of QCS69-SiO$_2$ was stronger than that of QCS93-SiO$_2$. This was in agreement with the flocculation results (Fig. 5).

In case of cationic starch-SiO$_2$ system, the turbidity of white water was increased with the dosage of SiO$_2$ when cationic starch was 3.2 mg/g of addition. This means that the dynamic drainage performance of cationic starch-SiO$_2$ system was lower on the higher addition of SiO$_2$. This phenomenon was also consistent to the flocculation. However, when cationic starch was added in 12.8 mg/g level, the turbidity of white water was, similar to that in QCS-SiO$_2$ system, decreased with the increasing of dosage of SiO$_2$. This was because the fiber substrates were still charged negatively as cationic starch was 3.2 mg/g of addition. As explained above, the addition of negatively SiO$_2$ increased the repulsion between the substrates such as the fines, the fibers and CaCO$_3$ filler. If cationic starch was overdosed, the ξ-potential of the substrates was positive value, and thus SiO$_2$ could interact with the adsorbed cationic starch, and like the above QCS-SiO$_2$ system, reduce the turbidity of white water.

The mechanism of flocculation by QCS-SiO$_2$ system

It is known that QCS is a polyelectrolyte containing cationic groups, hydroxyl groups, and primary amino groups. The bleached reed pulp substrates

contain hydroxyl groups, carboxylic acid groups, and aldehyde groups, 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 QCS and cellulosic substrates are electrostatic attraction and non-electrostatic interaction such as hydrogen bonding, Van der walls force, and covalent bonding (e.g., Schiff bases). Several earlier works[2,26] revealed that the interaction between QCS and bleached reed substrates was dominated by electrostatic forces, and the flocculation of reed pulp was patch mechanism.

Comparing the experimental results, it was reasonable to conclude that the flocculation mechanism of QCS-SiO$_2$ system was quite different from those achieved with the single-component (QCS) system. For single system, the adsorbed QCS was in a flat congregation with much less chain loops and tails, and formed positively charged patch on the substrates surfaces. These positively patch could attract the negatively charged patch that represent the original particle surface, and induced the patch flocculation to take place. After the flocs were broken at a higher shear, the reflocculation was not to occur in general.

However, SiO$_2$ acted as a bridging agent between cationic sites created by the cationic polymer when added to the pulp pretreated by QCS, and the nanoparticles and polyelectrolyte segments were able to form bridges far beyond the separation where the polyelectrolyte segments alone can bridge the surfaces, the system were likely to be much tougher, which could explain the higher shear resistance of polymer-nanoparticle systems compared with pure polyelectrolyte systems. Figure 10 showed the flocculation modes of dual-component (QCS-nano-SiO$_2$) and one-component (QCS) system.
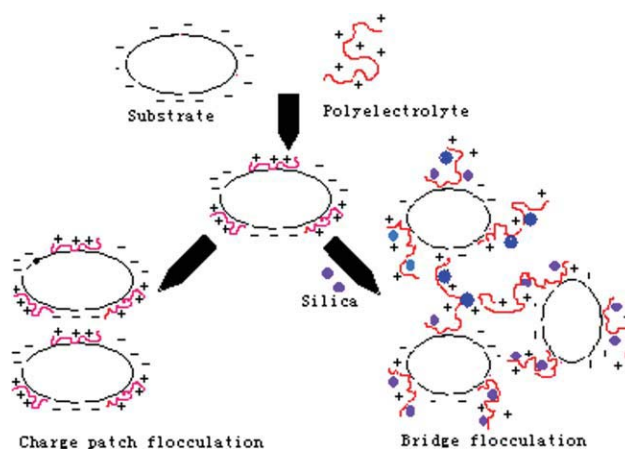
Figure 10 Flocculation mode of QCS-nanometer SiO$_2$ system. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

- QCS permeated into the porous fibers, and ξ-potential was fallen with the increasing time.
- Cationic polyelectrolyte–nano-SiO$_2$ could reduce the residual turbidity of white water, this was because that the adsorbed QCS chains were stretched out to aqueous media by nano-SiO$_2$, and adsorbed polyelectrolyte chains were more strong bridge flocculation. However, the dosage of polyelectrolyte should be passing the amount that was corresponding to the isoelectric point ($\xi = 0$ V).
- An increase in shear after an initial flocculation by QCS lead to floc breakage and this was showed to be beneficial for the flocculation by the addition of nano-SiO$_2$. i.e., the reflocculation could occur in the QCS- nano-SiO$_2$ system. The reason was likely to be a larger number of pre-adsorbed QCS molecules were available for interaction with nano-SiO$_2$.
- It has been showed that the effect on the fiber flocculation of electrolyte concentration in the QCS-nano-SiO$_2$ system was governed not only by the adsorption of QCS onto the substrate surface but also by the interaction between polyelectrolyte and nano-SiO$_2$ particle.

References

1. Gibbs, A.; Pelton, R.; Cong, R. Colloids Surf A: Physicochem Eng Aspects 1999, 159, 31.
2. Pal, S.; Mal, D.; Singh, R. P. Carbohydr Polym 2005, 59, 417.
3. Chi, H.; Li, H.; Liu, W.; Zhan, H. Colloids Surf A: Physicochem Eng Aspects 2007, 297, 147.
4. Wägberg, L.; Lindström, T. Nordic Pulp Paper Res J 1989, 2, 49.
5. Björklund, M.; Wågberg, L. Colloids Surf A: Physicochem Eng Aspects 1995, 105, 199.
6. Swerin, A.; Sjodin, U.; ödberg, L. Nord Pulp Pap Res J 1993, 8, 389.
7. Cherie, O.; Nicholas, W. Tappi J 2000, 83, 80.
8. Langley, J. G.; Litchfield, E. Dewatering Aids for Paper Applications Process, Tappi Papermakers Conf.; Atlanta, 1986; 89–93.
9. Andersson, K.; Sandström, A.; Barla, P. Noric Pulp Paper Res J 1986, 1, 26.
10. Swerin, A.; Risinger, G.; Ödberg, L. J Pulp Pap Sci 1997, 23, 374.
11. Lindström, T. Some fundamental chemical aspects of paper forming, in fundamental of papermaking, Trans. 9th Fundam. Res. Symp.; Cambridge, 1989; 309–313.
12. Stemme, S.; Ödberg, L.; Malmsten, M. Colloids Surf A: Physicochem Eng Aspects 1999, 155, 145.
13. Qin, C. Q.; Du, Y. M.; Xiao, L. Polym Degrad Stab 2002, 76, 211.
14. Sennerfors, T.; Fröberg, J. C.; Tiberg, F. J Colloids Interface Sci 2000, 228, 127.
15. Wägberg, L. Nordic Pulp Paper Res J 1989, 4, 135.
16. Scott, W. E. Tappi J 1993, 76, 123.
17. Li, H.; Du, Y.; Wu, X.; Zhan, H. Colloids Surf A: Physicochem Eng Aspects 2004, 242, 1.
18. Guppta, B. Interactions Between Cationic Starches and Papermaking Fibers: The Effect of Starch Characteristics on Fiber Surface Charge and Starch Retention, TAPPI Papermakers Conference: Chicago, Illinois, 1995; pp 85–91.
19. Swerin, A.; Ödberg, L.; Sjodin, U. Paper Technol 1992, 33, 28.
20. Van de Steeg, H. G. M.; Cohen Stuart, M. A.; De Keizer, A.; Bijsterbosch, B. H. Langmuir 1992, 10, 2538.
21. Wägberg, L.; Björklund, M.; Asell, I.; Swerin, A. Tappi J 1996, 79, 157.
22. Swerin, A.; Ödberg, L. Nordic Pulp Paper Res J 1996, 11, 22.
23. Unbehend, J. E. Tappi 1976, 59, 74.
24. Tanaka, H.; Swerin, A.; Odberg, L. Tappi J 1993, 76, 157.
25. Swerin, A.; Ödberg, L.; Sjodin, U. Flocculation of Cellulosic Fiber Suspensions by Microparticulate Retention Aid Systems. Chem Papermaking Conf. Proc.; Leatherhead, UK, 1991; paper 06, p 8.
26. Li, H.; Du, Y.; Xu, Y.; Zhan, H.; Kennedy, J. F. Carbohydr Polym 2004, 58, 205.