

## STUDYING THE EFFECT OF CATIONIC STARCH- ANIONIC NANOSILICA SYSTEM ON RETENTION AND DRAINAGE

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Nanoparticles are widely used in the papermaking industry as retention/drainage aids, usually in conjunction with a high mass cationic polyelectrolyte such as cationic starch. However, little convincing knowledge of their role and mechanism in the wet-end system is yet found. This work focused on the role of nanosilica on papermaking wet end system in response to some processing parameters (drainage, retention, and electrostatic force of the whole system). The observations indicated that the nanosilica performance is defined by interactions of nanosilica with the complex aqueous environment of wet end system. The interaction mechanism seems to rely on introduction of nanoparticles into a cationic starch-fines-fibers network, converting the fiber mat on the forming wire into a porous structure that is responsive to retention and drainage.

*Key Words: Nanoparticles; Zeta-potential; Fines; Microflocculation; Wet-end; Papermaking*

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### INTRODUCTION

The use of nanoparticles in papermaking has a long history. Papermaking technology, in terms of the amount of materials consumed, is already a leader in terms of the amounts of nanoparticles used (Hubbe 2005a). Papermakers employ nanosilica and related products each year to promote dewatering and fine-particle retention on hundreds of paper machines, but yet there are many areas of this technology that are unknown to papermakers (Carr 2004; Hubbe 2005b).

In recent years, among nanoparticles, anionic colloidal silica has been used the most (Aloi 1998). Table 1 shows characteristics of typical nanosilica (Wagberg and Solberg 2002). However, laboratory-made nanoparticles (organo-modified cationic silica nanoparticles or other nano-structured silicas and silicates) have also had papermaking applications (Xiao and Cezar 2003; Johnston et. al. 2004).

The influence of nanoparticles on drainage and retention in the presence of cationic polyelectrolyte has been frequently studied, but the mechanism by which nanoparticles contribute on drainage or retention is still no yet fully understood (Solberg and Wagberg 2003). Moberg (1993) proposed that colloidal silica is physically small enough to enter the amorphous structure of the cationic starch in solution to neutralize the

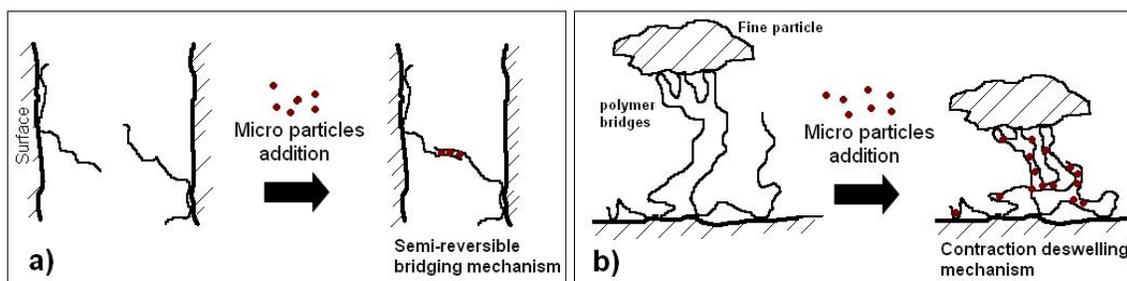
starch cationic charge, thereby compressing the electrical double layer, a prerequisite for retention. Aloï (1998) postulated that a proper ionic concentration from anionic microparticles to achieve near-neutrality of the electrical double layers in the system is a precondition for microfloculation (coagulation), thus retention. Solberg and Wågberg (2003) proposed that the contraction is based on replacing weak hydrogen bonds with strong ionic bonds, thus collapsing the flocs under their own weight, a reason for enhanced dewatering.

**Table 1.** Properties of Colloidal Silica Used by Wagberg and Solberg (2002)

	S.A.[m <sup>2</sup> /gr]	Size[nm]	L[nm]	W[nm]	C.D.[m eq./g]
Silica 1	620	4.4	19	6	0.152
Silica 2	640	4.5	54	7	0.136

- S.A. : Surface Area determined by titration  
 - Size : Primary particle size calculated from the surface area  
 - L : Ellipsoid long diameter  
 - W: Ellipsoid short diameter  
 -C.D.: Charge density based on polyelectrolytes titration at pH 5.6

To explain the role of interactions between microparticles and polyelectrolyte molecules on retention and drainage in pulp processing, Hubbe (2005) proposed a model depicted in Figure 1. The model is based on a bridging mechanism through cationic polyelectrolytes, but the presence of microparticles or nanoparticles in the system converts the system to a new type of bridging, which involves complexation between the polyelectrolyte and the nanoparticle. The combined additives then function simultaneously both as a drainage agent and also as a retention agent.



**Fig.1.** Schematic illustrations to show a) semi-reversible bridging mechanism and b) contraction deswelling mechanism (see Hubbe 2005)

The relation between nanoparticles' influence on drainage and retention with zeta potential has been studied previously (Miyanishi 1995; Penniman and Makhonin 1993). It has been proposed that nanoparticles are effective in retention or drainage if the whole system operates in a mildly positive charge zone (Hubbe 2005b). This hypothesis has also been examined in our laboratory using nanosilica with quaternary cationic starch by monitoring the changes in zeta potential of the suspension. The role of fines on the efficiency of nanoparticles in the wet end system was also explored

## EXPERIMENTAL

### Materials

The fiber furnish consisted of 85% bleached chemical eucalyptus and 15% bleached chemical softwood in the form of dry pulp, which were separately soaked in tap water with the conductivity of 0.33 ms/cm overnight, then disintegrated and beaten in a laboratory Hollander beater according to TAPPI T200 sp-96 procedure, up to 340 ml CSF and 470 ml CSF, respectively.

Quaternary cationic tapioca starch with DS: 2.5% and precipitated calcium carbonate with average particle size of 2.35 $\mu$ m, which was used as filler, were provided by Advance Agro paper mill, Thailand. The cationic starch was converted into solution form with 0.5% consistency and heated on hot plate about 30 min. up to 90°C. The solution was kept at this temperature for another 30 min, then moderately cooled to room temperature and used within one day. The anionic nanosilica sol was an Eka Chemical Company product (NP 882) having a high specific surface area and average diameter of 2-5 nm. Polyaluminum chloride (PAC), which is a common anionic trash catcher (ATC) containing 10% Al<sub>2</sub>O<sub>3</sub> equivalent, also was purchased from Eka Chemical Company.

### Methods

Evaluation of the first pass retention (FPR) was conducted using a Dynamic Drainage Jar (DDJ) according to the TAPPI T-261 cm-00 method. A furnish was developed using 80% of the stock (i.e., the original stock with 85% eucalyptus and 15% bleached softwood) and 20% PCC as filler, based on the following addition order: Polyaluminum chloride (PAC) at a dosage of 0.05% was added to the fiber furnish. The mixing rate was kept constant at 1000 rpm. At the same mixing rate, cationic starch, then PCC was added. To simulate the approach flow system, the mixing rate was reduced to 800 rpm, and then colloidal silica nanoparticles solution (NP) was added as the final component. All the addition intervals were one minute, except for nanoparticles mixing time, which was limited to only 15 seconds. For evaluation of the drainage value, the above mentioned procedure was followed, without filler addition. Then, the drainability of the pulp was measured using a Canadian Standard Freeness (CSF) tester according to TAPPI T-261 cm-00 standard. All the experiments were repeated under the same conditions, and the final furnish was rapidly transferred to a Mutek System Zeta Potential (SZP 06) to measure zeta potential based on streaming potential. For some experiments, the required fines-free pulp was prepared in a Bauer MC-Nett apparatus according to the SCAN-M6:69 procedure.

## RESULTS

### Cationic Starch Effect on Retention and Drainage

Retention is well related to drainage in pulp processing. In general, some of the fines, fillers, and other furnish components drain along with water in the forming stage, which loads process white water and brings about increases in production costs and waste handling problems. So, an increase of retention to a desired level is a critical stage in

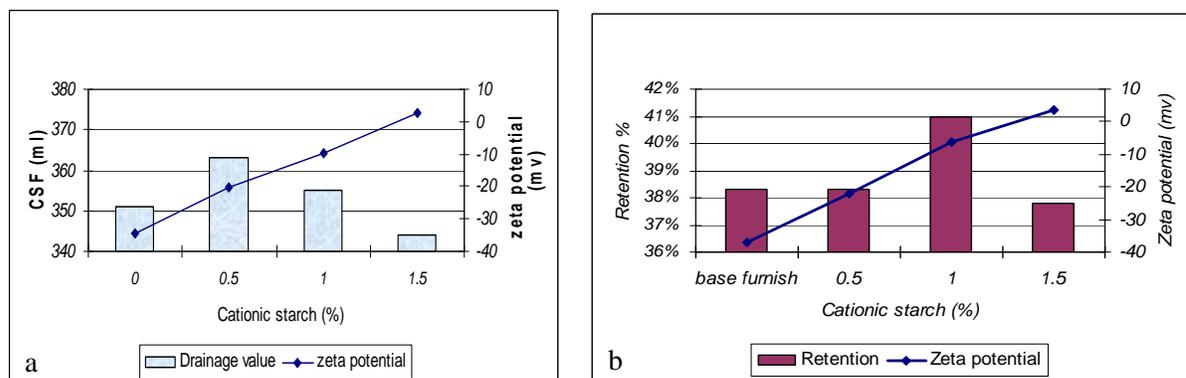
papermaking. Drainage is also equally important as retention due to the requirements of modern high speed paper machines. Fines swell in aqueous solution, thus reducing drainage capacity of the forming section, which represents the major step in the dewatering process. Swollen fines also fill the interstices among the fiber network in the forming section, thus slowing down the drainage process. Fillers do not swell and they are smaller than most cellulosic fines; thus in a furnish without swollen fines, the filler particles mostly pass through the forming web of paper with the white water stream. It is also worth mentioning that all the fines do not swell to the same degree. In this respect fillers and some of the cellulosic fines behave alike in an aqueous environment.

Retention aids agglomerate fines and fillers at the wet end system, thus enhancing retention and drainage. Agglomerated particles (i.e., assemblies of fines, fillers, sizing additives, etc.) are sufficiently larger in size to remain on the forming wire, reinforcing the retention. Retention systems (dual polymer systems or particulate systems) also increase drainage through restoring the original porous structure of the fiber network.

The increase in retention with addition of 0.5% long-chain cationic starch takes place due to adsorption of cationic starch macromolecular chains on the fines and fillers, thereby initiating microfloculation (Fig. 2b). The cationic starch initiates the microfloculation by establishing polymer bridges among the wet end system components. The neutralization of system charge due to the cationic starch may also assist bridging through diminishing the effect of the electrostatic double layer.

Retention showed a sharp increase at 1% cationic starch charge, where the zeta potential was yet in the negative zone (-10 mv), but it regained its original level if the starch dose increased to 1.5%. It seems that addition of starch, which contributed visibly in system charge, had no causal relation with retention (Fig. 2b). A similar observation has been reported by Xiang and Somasundaran (1996) earlier. The authors compared simple polymer microfloculation with dual polymer microfloculation using alumina (aluminium oxide powder,  $\text{Al}_2\text{O}_3$ ). Unlike a single polymer system, no correlation was found between zeta potential and microfloculation, highlighting the fact that in a complex system the electrostatic force is not the only governing force in the system.

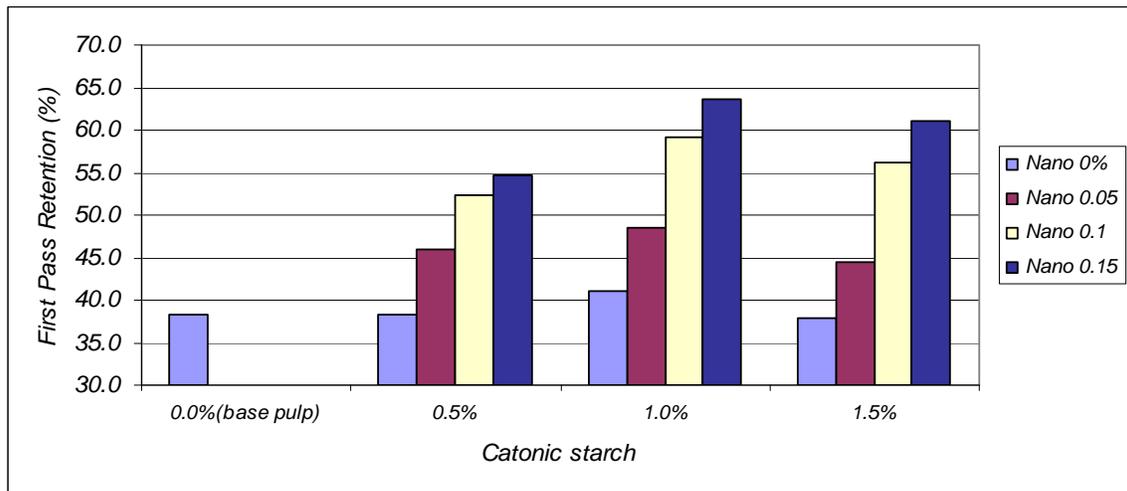
Comparing Figs. 2a and 2b suggests that although the cationic starch contributed to retention, its contribution to drainage was marginal, highlighting the fact that the cationic starch by itself is not a strong drainage aid.



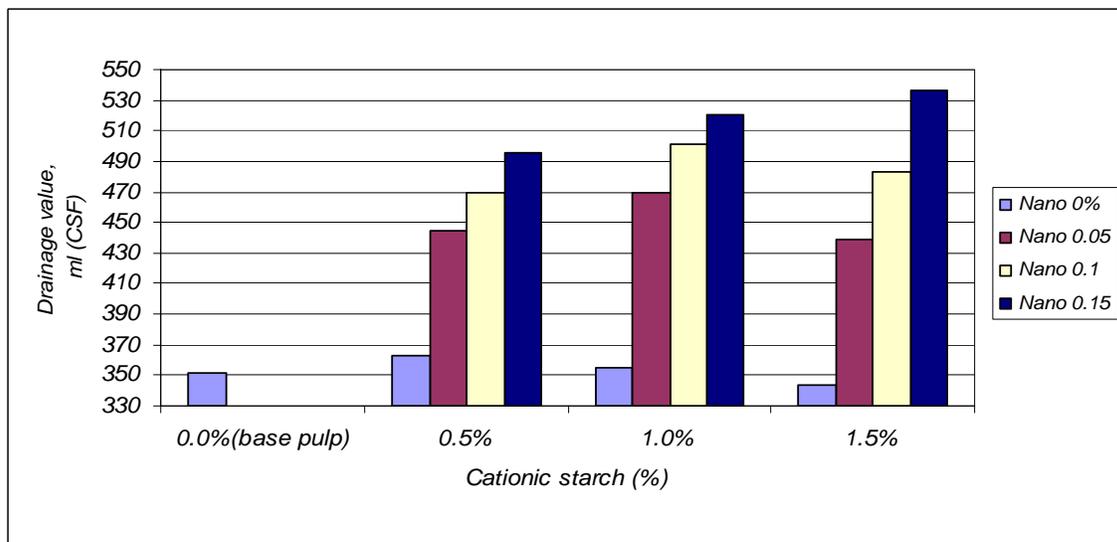
**Fig. 2.** Influence of cationic starch on a) drainage (without filler), b) first pass retention (PCC: 20%, fines: 16.7 %) versus zeta potential

### Nanoparticles Effect on Retention or Drainage

Figures 3 and 4 also suggest that the influence of cationic starch on retention and drainage was marginal, but both the drainage and retention were almost doubled if nanoparticles were injected into the system. The higher the nanoparticles dosage, the better was the drainage or retention. It seems that both drainage and retention reached to their maximum at 1% cationic starch dosage. Further increase in the cationic starch dosage did not show any sizable change on either retention or drainage. At a 1.5% addition of cationic starch, compared to 1.0% addition, the retention as well as the drainage were even slightly reduced for all levels of nanosilica addition, except for drainage at 0.15% dosage (See Figs 3-4).



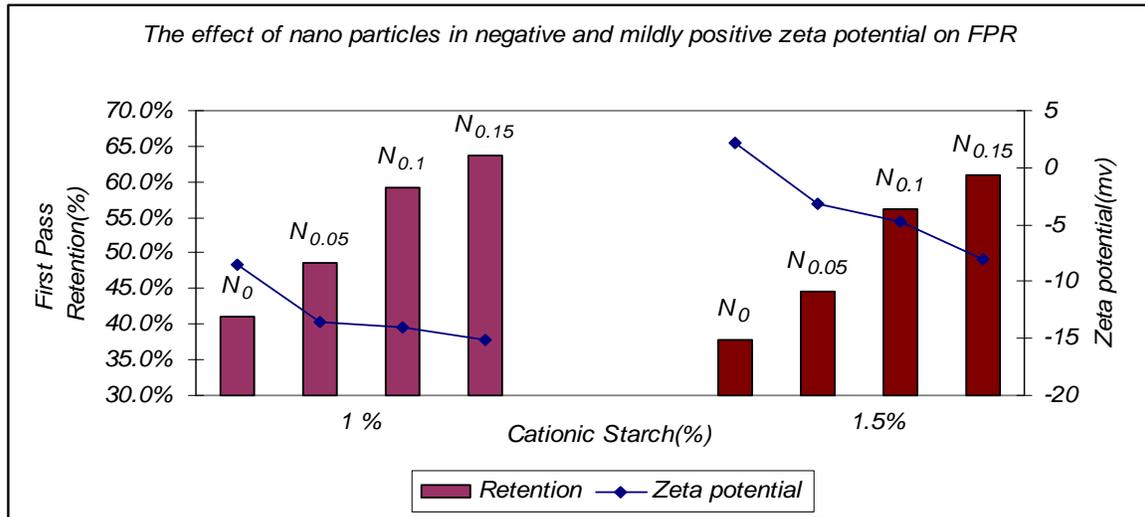
**Fig. 3.** Influence of nano silica on First Pass Retention (FPR) in fine paper furnish (PCC: 20%, fines:16.7 %) with different cationic starch levels



**Fig. 4.** Influence of nanosilica on drainability of the pulp with different cationic starch levels

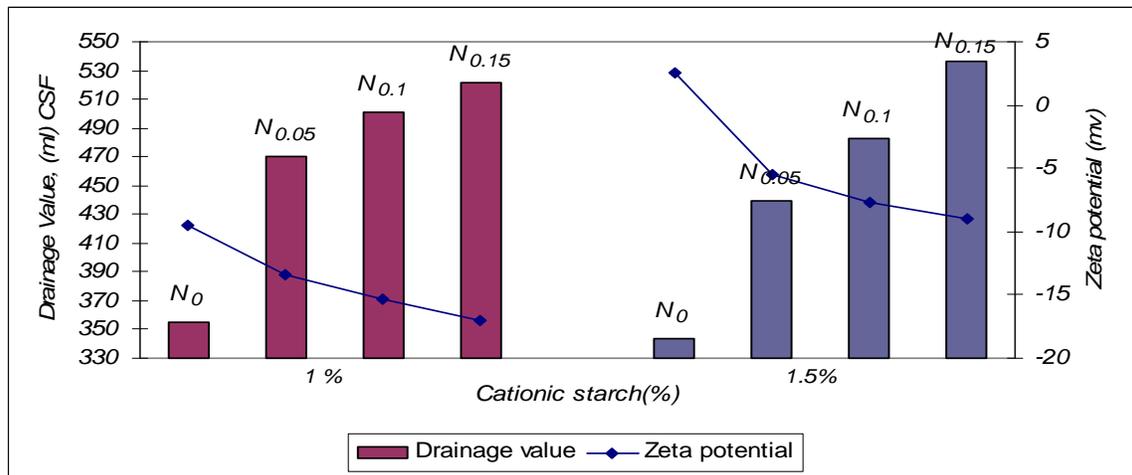
**Nanoparticles Addition Point**

Reversing a system zeta potential from negative to positive has been reported as an effective method of nanoparticles application in the wet-end system (Miyanishi 1995; Penniman and Makhonin 1993). This hypothesis has also been examined in our laboratory, and the results are reported in Figs. 5 and 6.



**Fig. 5.** The relation between retention, nanoparticles effect, and zeta potential (in fine paper furnish with 20% PCC, N: nanoparticles dosage %)

Figures 5 and 6 show that, prior to addition of nanoparticles, the zeta potential was either in a negative zone (for 1% starch dosage) or in a positive zone (for the starch charge of 1.5%).



**Figure 6:** The relation between drainage, nanoparticles effect and zeta potential

Although the differences for either retention or drainage were marginal, Figs. 5 and 6 show that both retention and drainage were slightly better for 1% cationic starch dosage compared to 1.5% cationic dosage for all levels of nanoparticles addition (0.05%

up to 0.15%), except for drainage at a nanoparticle addition level of 0.15%. This is an expected outcome due to the fact that both experiments were conducted in the vicinity of the isoelectric point (i.e.,  $\pm 5$  mv), where the double layer effect is at its lowest stage. Thus, it could be concluded that the effective strategy for charging nanoparticles to adjust the dosages of additives so that the system is near its isoelectric point.

### Fines and Nanoparticles Interactions in Wet-end System

In order to study the interaction between fines and the nanoparticles system, a fines-free pulp was prepared using the Bauer McNett classifier, then a wet end system including nanoparticles as reported in the method section was applied. As Fig. 7 shows, the freeness of fines-free pulp was about twice that of the whole pulp (i.e. pulp including fines), which suggests that the fines are the main cause of drainage loss. An aqueous environment indeed swells the fines. The swollen fines diminish the drainage through blocking the interstices of the fiber network. Unlike the fines, fillers are able to pass through the network pores with ease, which can create a high load on the white water stream (Lin et al. 2007).

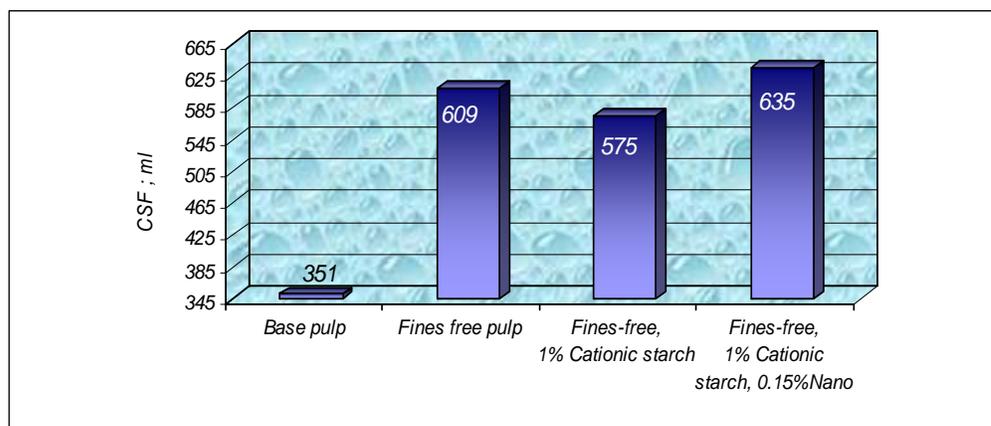


Fig. 7. Drainage of fines-free pulp and no drastic nanoparticles effect

Cationic polyelectrolytes along with nanoparticles influence drainage or retention through agglomeration of fines or fillers. The agglomeration of fines partially restores the fines-free pulp pore structure through collecting the fines that were blocking the fiber-mat pores on the forming wire, thus enhancing the drainage. It seems that retention in a furnish that includes fines (specially the fines generated by refining) is well correlated with the drainage. Harrington and Schuster (1996) as well as Baron et al. (1990), even though they used a dual polymer system for retention, yet reported an increase in drainage. Lewis and Polverari (2006) using micropolymer with either polyacrylamide or fine particles reported an increase in drainage as well as retention. These observations further highlight the fact that the retention is well related to drainage, and the observed increase in drainage for the cationic-nanosilica system could not be attributed to the nanoparticles alone.

Figure 7 also shows that neither the addition of cationic starch nor that of nanoparticles, as a sole additive, was able to influence the drainage. These results

suggest that wet end additives alter the network structure through controlling the fines or fillers rather than fibers.

## **DISCUSSION**

### **Retention**

Retention in a paper machine wet end depends on aggregation (coagulation or microfloculation) of fine particles (fines, fillers, sizing additives, etc.) and adsorption of these aggregates on fiber surfaces. A good retention system promotes the adsorption of aggregates on fiber surfaces, and it simultaneously avoids excessive flocculation (aggregation of fibers). Fiber flocculation is detrimental to paper formation uniformity. Formation uniformity is a major requirement for paper printability. For cationic linear polymers of high molecular weight, adsorption on fine particles or cellulose fibers occurs either through a bridging mechanism (anchoring at different surfaces) or charge neutralization. The entropy of the system is the main cause of the anchoring (Tilberg et al. 2001), although charge neutralization also contributes in anchoring the polyelectrolytes on fiber or fine particle surfaces, and electrostatic forces can enhance the height of loops and tails of the polyelectrolytes relative to the surface where they are attached. This is the main reason for use of high molecular weight cationic polyelectrolytes in a papermaking wet end system. For flocculation to take place, the length of the tails or loops of a molecule should exceed the effective thickness of the electrostatic double layer. In the case of low molecular weight polyelectrolyte application, the double layer thickness should be first suppressed by addition of salt. Charge neutralization occurs in the vicinity of zero potential (i.e., the isoelectric point), where the aggregation of fine particles (i.e., fines, fillers, sizing additives) is at its maximum point. It is reported that the electrostatic aggregation, unlike polymer bridging, is sensitive to shear forces (Tiberg et al. 2001). The shear imposed in wet end is far in excess of the electrostatic binding energy.

### **Polymer Behavior in Suspension**

Polymers in the solutions behave differently depending on the polymer charge density, polymer molecular weight, affinity of polymer to the solvent, and the concentration of ions in the solution. In a solution with low ionic density the polymers that have a long chain, but relatively low charge density adopt a random coil conformation. The radius of gyration is an indicator of the size of these macromolecules in their coiled conformation. Cationic starch is a like-charged polyelectrolyte. The presence of like-charges on the backbone of the polyelectrolytes generates electrostatic repulsive charges, resulting in an extended conformation. Highly charged polyelectrolytes at an environment with a very low ionic strength behave like a stiff rod (Tilberg et al. 2001).

### **Nanoparticles' Role in Retention**

Addition of silica to a wet end system (i.e., a system composed of high molecular weight cationic starch, fibers, fines, fillers, and polyaluminum chloride (PAC)) almost

doubled both retention and drainage - 65% and 500 ml respectively. This is a striking achievement, which probably relates to the properties specific to the behavior of particulate materials in the vicinity of polyelectrolytes in an aqueous solution.

The long-chain cationic starch adsorption on the surfaces occurs through either bridging or charge neutralization, as it has been highlighted earlier. The presence of the starch, especially the amylopectin component, in the system assists anchoring the starch on fibers, fines and fillers. Adsorbed amylopectin molecules have a more open structure, since more space is required at each branching point. Charge neutralization promotes the bridging through depressing the double layer thickness.

Anionic nanosilica sol, as used in the present experiment, has a remarkably high specific surface area (i.e., about 600 m<sup>2</sup>/g, as estimated from nanoparticles average diameter). Thus, nanosilica neutralizes the polyelectrolyte charges more aggressively than the other anionic components of the wet end system. Adsorption of nanosilica particles screens out repulsive electrostatic interactions between the polymers and the surfaces, thus increasing the adsorption.

The presence of fines in a papermaking furnish facilitates the aggregation process. It was earlier demonstrated (see Fig. 7) that neither cationic starch nor anionic silica by itself contributes to retention or drainage of a furnish that is free from fines. Therefore, fines or fillers are more prone to aggregation than fibers. This is advantageous for retention aids. The retention aides could increase retention without deteriorating the formation through flocculation (namely agglomeration of fibers).

Aggregation of fines, fillers, and anionic nanosilica may have also been promoted by hydrophobic forces generated by non-electrostatic interactions of the system.

## CONCLUSIONS

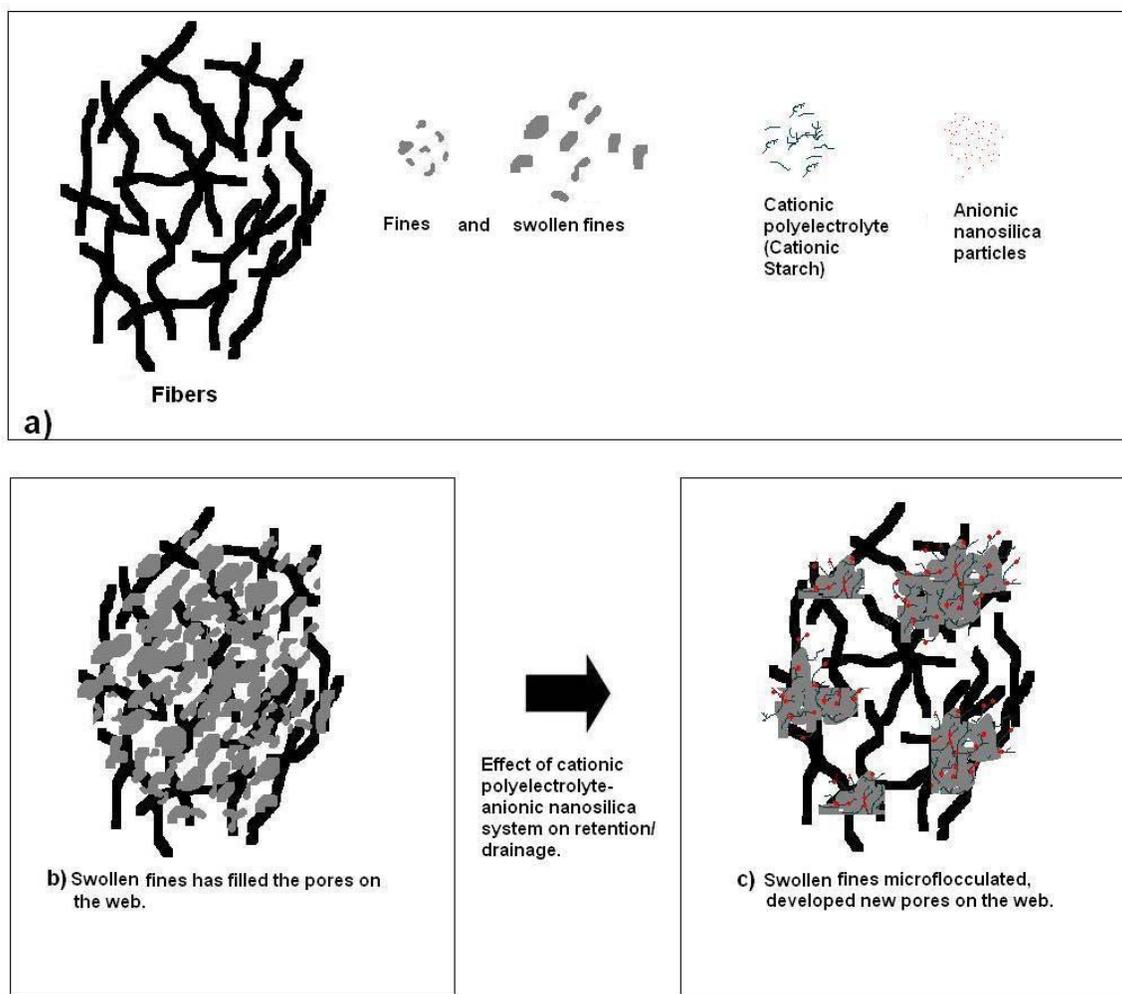
High molecular weight cationic starch by itself slightly increased retention (by about 5%), but its influence on drainage was almost nil. A correlation between zeta potential variation and retention or drainage was not found.

Anionic nanosilica particles, unlike cationic starch, played a significant role in retention and drainage, but only if it was used in a system that contained high molecular weight cationic starch. The retention or drainage gains were at a scale of 25%. The mechanism responsible for the gain was assumed to be bridging and charge neutralization. It was inferred that bridging played a significant role in the development of microfloculation.

Addition of fine particles (i.e., nano or micro-particles) to a system including high molecular weight cationic polyelectrolyte further activated the bridging mechanism. Based on this understanding we recommend that the cationic polyelectrolyte should be added to the wet end system prior to fine particles.

It was concluded that microfloculation (i.e., fines and fillers aggregation through high molecular weight cationic polyelectrolyte) is responsible for the observed gain in retention and drainage. Microfloculation through agglomeration of fines and fillers converts the wet end network to an open network similar to a fines-free network, thus

making the system responsive to both retention and drainage. A schematic representation of this understanding is given in Figure 8.



**Figure 8.** Schematic representation of Cationic polyelectrolyte-Fine particles system effect on retention and drainage

## ACKNOWLEDGEMENT

The authors express their appreciation from Asian Institute of Technology (AIT) authority, specifically professor Said Irandoust (AIT president) for his support of the project, Pulp and Paper Technology of AIT for providing intellectual and technical support, Advance Agro of Thailand for providing nanoparticles, Dr. Kolmodin, H. of Advance Agro for intellectual contribution. The authors also thank Professor Martin A. Hubbe of North Carolina University for comments during the execution of the project.

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Article submitted: February 8, 2010; Peer review completed: March 10, 2010; Revised version received and accepted: March 19, 2010; Published: March 25, 2010.