Utilization of Cationic Starch- Nano Silica Dual System to Improve Zeta Potential, Retention, and Drainage of Mixed NSSC - OCC Pulp

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Today, utilization of new technologies in different industries has gained paramount importance. With expanding nanoparticles applications during recent years, the use of these particles together with some commonly used high molecular weight poly-electrolytes has received considerable attention for improving the retention of fine and fillers in paper industry. This study is a review on the effect of using anionic nano-silica particles and cationic starch as a dual system on important wet end parameters such as zeta potential, retention, and drainability. The results showed that adding cationic starch to the mixture of 20/80 Neutral Sulfite Semichemical pulp (NSSC) and old Corrugated Container (OCC) increased the rate of retention. Moreover, dual usage of cationic starch and nano-silica particles improved the maximum retention rate at all addition levels. By contrast, addition of 1.8% cationic starch along with nano-silica particles decreased the drainability. This result can be attributed to the insufficient amount of cationic starch in the system. However, it enhanced drainage at the addition level of 2.2%. The maximum rate of drainage was obtained from the treatment containing 2.4 % cationic starch and 1 % nano-silica.

Keywords: Colloidal nano-silica; Cationic starch; NSSC and OCC; Zeta potential; Retention; Drainability

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INTRODUCTION

Nano particles utilization in paper manufacturing industry has a long history, and paper manufacturers utilize nanoparticles for the purpose of maintaining fiber's particles in paper machines (Hubbe 2005b). In many regions, utilization of nanoparticles is unknown for many paper manufactures (Hubbe 2005c), but in recent years, use of nanoparticles, including anionic colloidal silica, has been increased (Aloi 1998). Thus, some researchers have studied the subject of utilizing nanoparticles in the wet-end of pulp and paper industry (Carr 2004; Weise *et al.* 2000; Lowry 2006; Hubbe 2006) and reported that usage of nano-silica together with cationic starch and cationic polyacrylamide can have a positive effect on paper properties.

By extension of utilizing particles at nano dimensions with very high charge density, the possibility of improving the retention of fine and fillers and also increasing the rate of drainage has been achieved. In addition to the improvement of retention and drainability, other privileges such as increasing the dry strength of papers has been claimed, resulting from retention increase or increasing the cationic starch efficiently, increase of machine speed, reduction of stoppage times, increase of fiber's dispersion homogeneity, and chemical oxygen demand (COD) reduction of the mill's effluents (Gess 1998; Scott 1996; Carr 2004; Hubbe 2005c).

In general, the execution method when using these systems is such that cationic polymers are added to the pulp at the early stages of the papermaking process, and large coagulations of particles, which have been formed due to the addition of polymers, are broken by the shear stresses imposed during the next stage. Then, anionic particles at nano dimensions are added shortly before the paper sheet formation process (Wågberg *et al.* 1996). Also, some reports have been published regarding change of surface charges of nanoparticles and their laboratory usages in the form of cationic particles (Xiao and Cezar 2003).

Generally, cationic and/or polyacrylamide have been utilized as cationic polymers and on the other hand, anionic nano-silica (in the form of gel) and/or bentonite have been used as a component of which one dimension is within the nano limit (Miyanishi 1995; Gess 1998; Rodriguez 2005). Hubbe (2006) suggests that utilization of nano particles in the wet end improves retention and drainage processes. The researchers suggest two mechanisms for function of nano particles which include semi-irreversible bridges and contraction co-elongation (Figs. 1 & 2).

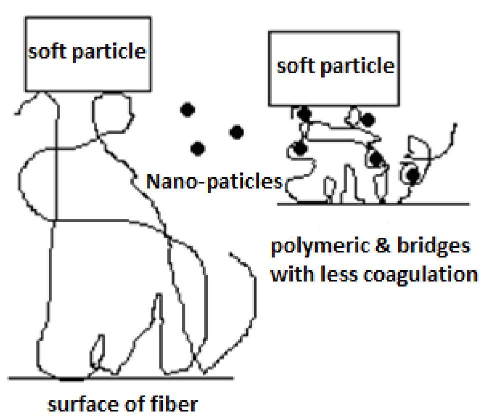

Fig. 1. Nanoparticle interactions resulting in the shortening of polymer bridges (Hubbe 2005b)

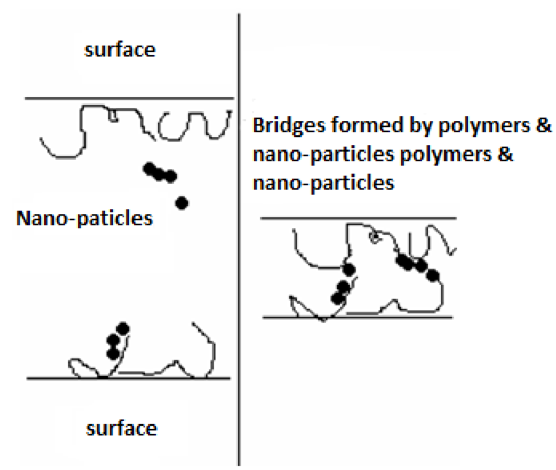

Fig. 2. Phenomena of forming semi irreversible bridges (Hubbe 2006)

The present study evaluates the effect of cationic starch and potential changes of NSSC pulp zeta potential on the efficiency of anionic silica nanoparticles with regard to drainage and retention capacities. It is worth mentioning that different studies have been conducted regarding utilization of anionic polymers together with nanoparticles. (Anderson 1984; Bon 1985; Eckland and nindestrom 1991; Booboo and Rotar 2005; Esodberg 2006; Khosravani 2009). Although various reviews have been performed in this area, but there are still many unknown and vague points.

EXPERIMENTAL

Mixture of 80% NSSC and 20% OCC (The 20/80 Mixture)

The studied pulp contained 80% NSSC and 20% OCC. The NSSC was prepared from Mazandaran Wood and Paper Industry (MWPI). The OCC paper was cut to small pieces and soaked in water for 24 hours. The pulp with 12% consistency was defibrated at 3000 rpm and up to 300 revolutions to reach the freeness of 430 mL CSF according to TAPPI 227 om-94 method.

Cationic tapioca starch from Siam modified starch Co's in Thailand and with the trade name of Excelcat 160 was used in the present research. This starch contains anionic tertiary amine group and approximately 4 units of cationic amine per each unit of Glucose anhydride.

The cationic starch preparation was carried out by placing a 1% starch solution on an electrical heater and then slowly heating of the solution to 90 ^{o}C for 30 minutes. After cooking of the starch, it was kept to be cooled down to the room temperature, and then the prepared solution was utilized during the same day for carrying out the related tests. Two levels of starch as 1.8% and 2.4% based on oven-dry weight of pulp were considered for the study.

As the NSSC pulp basically contains large amounts of anionic trash, which can have negative effects on the effectiveness of retention aids, and considering the easy access to aluminum sulphate (alum) at MWPI, it was used as a neutralizer for NSSC pulp anionic trash at the constant level of 1 % based on oven dry weight.

The nano-silica particles with the trade name of NP 440, manufactured by EKA Nobel Company, were obtained in powder form from Advance Agro paper manufacturing mill in Thailand and were prepared in the form of a 15% colorless solution.

This substance contains silica-gel particles with high specific gravity and high anionic charges and the dimensions of about 5 nanometers. For utilizing the nano-silica particles in the present research, a 1% solution of the same was prepared and was then added to the pulp stock at two levels of 1% and 1.7 % based on oven dry weight of pulp.

Zeta Potential

By utilization of zeta potential meter unit (Mutek SZP) which is called "Zeta potential system" (BTG Corp.), the capability of suspension was measured with the consistency of 0.3 to 3 % at different addition levels of starch and nano-silica.

Assessment of Retention in the First Pass and Drainage

In the dynamic drainage container (DDJ) which is called the "Dynamic Drainage Tester", the efficiency of retention of fine particles (*i.e.* the first-pass retention) and the rate of drainage were evaluated according to the recommended method of pulp and paper laboratory at Finland's Aalto University.

RESULTS AND DISCUSSION

The Effect of Cationic Starch and Anionic Nano-silica on Zeta Potential

The results of utilizing nano-silica at two loading levels of cationic starch as 1.8% and 2.4% are presented in Table 1. In the real wet-end system of paper manufacturing process, considering the high electrical conductivity capabilities of white water and the presence of anionic trash, increasing the zeta potential toward zero are progressed slowly. It is generally believed that retention and discharge capabilities are improved when zeta potential is almost zero, but in cases of using coagulating polymers with high molecular weights, this may not always hold true. In case of long chain polymers, where connections between the adjacent surfaces are made with bridging mechanism, charge neutralization can be of less importance (Hubbe 2005a). Table 2 shows that after adding alum and starch to the system, the zeta potential was changed from -9.3 to -7.1.

The addition of nano-silica particles to the pulp at a constant level of cationic starch causes the zeta potential to become more negative, which is in good agreement with the results of previous literature (Penniman 1993; Makhonin and Miyanishi 1995; Shigeru and Miyanishi 1997). It has been reported that nanoparticles show better efficiency in a system with a little positive charge. This can be achieved by adding cationic polymers prior to the addition of nanoparticles. The system charge will then return to the negative region following the addition of nanoparticles.

Table 1. The Effect of Cationic Starch and Nano-silica Particles on Zeta Potential of Mixed NSSC-OCC Pulp

Zeta potential	Treatments	Source
-9.3	NSSC (80) + OCC (20)	1
-8.9	NSSC (80) + OCC (20) + ALUM(T3)	2
-7.1	NSSC (80) + OCC (20) + ALUM + STARCH (1.8%)	3
-7.6	NSSC (80) + OCC (20) + ALUM + STARCH (1.8%) + NANO-SILICA (1%)	4
-7.7	NSSC (80) + OCC (20) + ALUM + STARCH (1.8%) + NANO-SILICA (1.7%)	5
-5.7	NSSC (80) + OCC (20) + ALUM + STARCH (2.4%)	6
-5.9	NSSC (80) + OCC (20) + ALUM + STARCH (2.4%) + NANO-SILICA (1%)	7
-6.2	NSSC (80) + OCC (20) + ALUM + STARCH (1.8%) + NANO-SILICA (1.7%)	8

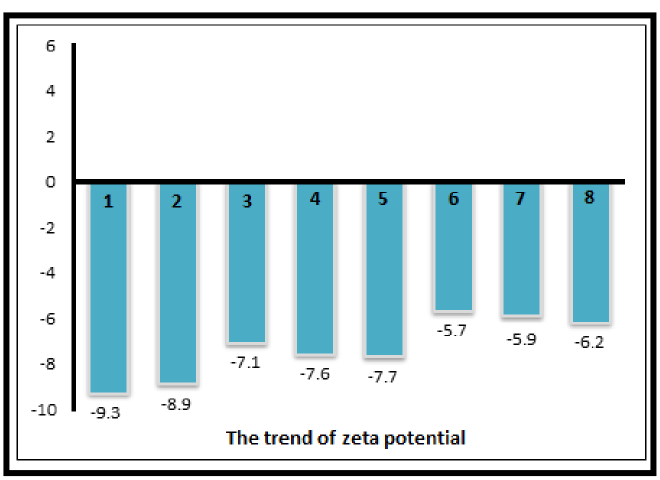

Fig. 3. The effect of cationic and Nano-silica treatments on zeta potential of the pulp

First Pass Retention

Reports indicate that changes of zeta potential of a system from negative to positive is an effective method for utilizing nanoparticles in the wet-end system (Miyanishi 1995; Penniman and Makhonin 1993).

As it is observed in Fig. 2, first pass retention was increased by adding cationic starch at both levels of 1.8% and 2.4%. However, this increase was more evident at the loading level of 2.4% cationic starch. In addition, with the dual system of cationic starch and nano-silica, even more progress in the first pass retention was observed (Table 2).

Silica colloidal particles are small enough to enter the structure of cationic starch and neutralize the starch charges. This phenomenon can collapse the dual electrical layer of silica/starch ion and form a small coagulation.

As such, the soft particles adsorbed by starch molecules will also enter the structure of this collapsed coagulation. As a matter of fact, anionic silica particles provide the possibility of increasing the retention by penetrating into the floc structure and contributing to the possibility of bridging and connecting the soft particles and the fillers that are attached to them. In general, polymers with high molecular weights are adsorbed preferably by the fiber flexible surfaces, such that only a part of their chains lies on the surface and the other parts are in the suspensions which have the form of strings or loops. These stringy parts can create a bridge and connect the soft particles together to form large scattered coagulations. After adding the nanoparticles, some parts of them lie between the separated and broken polymeric strings, providing the possibility of reforming the collapsed bridges, such that by penetrating another part of nanoparticles to the polymers structures, the polymers become compacted. Therefore, smaller coagulations can form. As a result, based on these effects of nanoparticles on the cationic polymer's structure, improvement of retention will be justified.

Table 2. Average Values for Retention and Drainage of Different Treatments.

Drainage	First Pass retention (%)	Treatments	
17.6	90	Non-Alum	NSSC (80) + OCC (20) + (1 %) Alum
20.9	90.2	With Alum	
31.3	93.5	Cationic starch 1.8%	
29.2	93.8	Cationic starch 1.8 % + Nano-silica 1 %	
25.3	94.6	Nano-silica 1.7 % + Cationic starch 1.8 %	
32.8	95.8	Cationic starch 2.4 %	
44.4	96.4	Nano-silica 1 % + Cationic starch 2.4 %	
43.4	96.3	Nano-silica 1.7 %+ Cationic starch 2.4 %	

After comparing 1.8% and 2.4% addition levels for the cationic starch, the result confirms the reports of some previous researchers (Bhardwaj *et al*. 2005; Rodriguez 2005) regarding the positive effect of approaching zeta value to zero. If the zeta potential is taken into consideration after adding nano-silica, the trend will be descending, whereas the retention will be improved. This observation is contrary to the above mentioned researcher's opinions (Bhardwaj *et al.* 2005; Rodriguez 2005) suggesting that the value of almost zero for the zeta potential is an important factor for better function of retention aids.

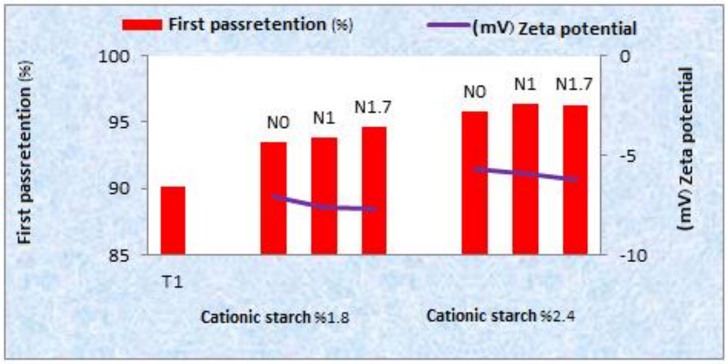

Fig. 2. The effect of different Nano-silica (N) and cationic starch treatments on the values of zeta potential and the first pass retention.

Pulp's Drainage Ability

As it is observed in Fig. 3, by adding cationic starch to the pulp, the drainage ability was increased. In fact, small and scattered coagulations are formed by the addition of cationic starch, which increase the outlet space. However, adding the constant amount of 1.8% starch together with nano-silica particles decreased pulp's drainage. This may have been a consequence of an insufficient amount of cationic starch in the system. But at the 2.4% addition level of cationic starch, drainage ability increased with the addition of nano-silica. In fact, the effect of nano-silica on drainage ability has been more evident in the treatments containing more cationic starch, which shows the mutual effect between cationic starches and nano-silica. Therefore, the important point about using nano-silica particles together with cationic starch is the necessity of preparing an excess of cationic charge in the system so as to provide the absorption possibility of nano-silica particles to creating fine and hard coagulations and free spaces in the pulp, which improve pulp's drainage ability. The effect of nano-silica particles on drainage ability can be related to the high charge density and its small dimensions.

In other words, after connection of soft particle together and to the fiber by cationic starch, the nano-silica small particles provide the possibility of penetrating into the cationic starch structure. On the other hand, the high charge density of these particles causes contraction and co-elongation of the structures, reducing their ability to keep water. If system's function on the zeta potential is reviewed before adding nano-silica and after adding cationic starch, in comparison between 1.8 and 2.4% loading level of cationic starch, the results confirm the opinions of some researchers (Bhardwaj *et al.* 2005; Rodriguez 2005) regarding the effect of approaching zeta to zero. If we pay attention to the zeta potential of the pulp after adding nano-silica, the trend is descending, but drainage has been improved. This is contrary to the opinions of the previous researchers who believe that approaching zeta potential to zero is an important factor for better function of chemicals. The reason is the presence of different nature of cationic starch nano-silica system, compared with other additives.

The highest drainage ability was observed in the treatment with 2.4% starch and 1% nano-silica, and the lowest one in the basic treatment without either starch or nano-silica.

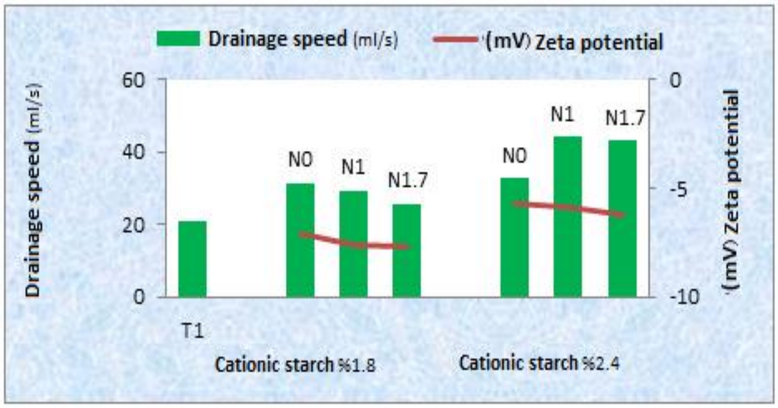

Fig. 3. The effect of different Nano-silica (N) cationic starch treatments on the values of zeta potential and drainage ability

In the figure, the significance of mutual effect of cationic starch and nano-silica shows the changes in the trend of drainage ability. Addition of 1% nano-silica together with 2.4% starch achieved maximum drainage ability. This point shows that similar to retention, the best function of this system, in terms of drainage ability occurred in a similar ratio of cationic starch to nano-silica.

CONCLUSIONS

In general, cationic starch is a strengthening additive for paper in dry condition and does not have a considerable effect on drainage ability and retention of soft particles and fillers by itself. Although addition of a little amount can slightly improve drainage ability by accumulation and coagulation of particles, addition of higher dosages increases water holding capabilities in the soft particles and reduces drainage ability.

With respect to the effect of cationic starch on pulp retention, zeta potential can be considered as a key factor for determining the suitable dosages of cationic polymers. In another word, considering that cationic starch is mostly adsorbed by the fibers; therefore the anionic wastes and conductive capacity of pulp are higher than cationic starch with higher DS (which has a better adsorption). Hence, because of the mentioned differences in various systems, we cannot find a universal optimum value for cationic starch, but we can use zeta potential as suitable criteria for determining the optimum dosage of cationic starch in the system, such that zeta potential is always less than iso-electric (zero zeta potential) point. The findings of present study indicate that the addition of nano-silica particles to the mixed OCC-NSSC pulp containing cationic starch increases drainage ability and retention. In fact the interactions between cationic starch and nano-silica and resultant zeta potential changes do not have an easily predictable effect on drainage and retention. Because by adding more nano particles, the retention and discharge capacities increase, while zeta potential deviates from the iso-electric point.

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