The Potential of Nanosilica – Cationic Starch Wet End System for Applying Higher Filler Content in Fine Paper

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Multiple studies have considered the nanosilica-cationic starch system to be a retention/drainage aid; however its potential to improve strength has previously been neglected. This research focused on the effect of both nanosilica and cationic starch on certain crucial physical and mechanical properties of fine paper compared with a paper sheet containing no additives to evaluate how this system can compensate for using more filler in fine paper. In previous studies, it was suggested that the cationic starch-nanosilica system induces much tinier flocs and thus possibly results in better strength properties. In this respect, results revealed that cationic starch did, however, improve tensile index; this effect weakened at higher filler levels. Cationic starch and nanoparticles both improved internal bonding, while cationic starches' effect was more prominent. With more filler, tear index suffered. Although addition of cationic starch partly compensated this negative effect with filled papers, nanoparticles did not seem to have an obvious effect. Therefore, cationic starch provided the limited potential of using more filler and nanoparticles may do it indirectly.

Key Words: Nanoparticles; Cationic starch; Filler; Microflocculation; Wet-end; Paper strength

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INTRODUCTION

Papermakers have long been motivated to use the highest filler content possible without it having negative effects on paper strength properties. The economical benefits and optical improvements of having higher filler loading in paper can only be achieved if the increased filler loadings can be retained in the sheet. Therefore, two problems are usually associated with the use of fillers. First, fillers added to fibers suspended in water are not readily retained in the forming sheet because they are often too small to be mechanically entrapped; also, filler particles, fines, and fibers are usually negatively charged, so they repel each other and are not well retained. Second, filler particles interfere with the fiber-fiber bonding; therefore, the strength of the filled paper suffers (Al-Mehbad 2004; Chen *et al.* 2011).

To solve the first problem, highly efficient nanoparticle retention/drainage aid systems are available. The influence of nanoparticles on drainage and retention and the system optimizations in the presence of cationic polyelectrolyte has been frequently studied (Moberg 1993; Miyanishi 1995; Hubbe 2005; Khosravani *et al.* 2010).

There are also some reports on strength improvements as a result of nanoparticle system application. Hubbe (2005) reviewed a wide variety of studies on the benefits of using nanoparticle systems in the wet-end and listed the results in order of how often they had been mentioned in the literature. The resulting list showed the most widely claimed benefits of nanoparticle systems to be as follows: increased retention and drainage, improved formation, dry strength improvements, and increased solids after wet pressing.

Nilsson and Carlson (1993) believed that microparticle programs based on cationic or amphoteric starch result in strength improvements. They also expressed that cationic starch adsorption increased as nanosilica dosage was added, which could be a key reason for strength gains.

Moberg (1993) stated that the subject should be considered differently for the bentonite and colloidal silica systems. In the case of a bentonite-based microparticle system, it can be run with or without cationic starch, since such programs typically employ a cationic synthetic polymer. When starch is not used, the bentonite system is expected to have little direct effect on strength. There is, however, an indirect effect, in which improved dewatering, on some machines, can be used to increase refining, thereby gaining strength indirectly. This is especially important on board machines, for which machine speed is often limited by refining levels. In the case of the nanosilica system considered, since starch was an integral part of that system, dry strength was directly affected, although the system increased dewatering and this effect also can be used to increase refining for improved strength.

All of the above-mentioned reports indicate the potential of a nanosilica/cationic starch system to improve retention, drainage, and strength. But, in terms of strength, there is little knowledge based on experimental data about how effective the system is in this area. Hence, this study focused on the potential of the common nanosilica/cationic starch system to compensate for the negative effects of using higher filler content in fine paper.

EXPERIMENTAL

Materials

The fiber furnish consisted of 85% bleached chemical eucalyptus and 15% bleached chemical softwood in the form of dry pulp, which was separately soaked in tap water with a conductivity of 0.33 ms/cm overnight, then disintegrated and beaten in a laboratory Hollander beater according to TAPPI T200 sp-96 procedure, respectively, up to 340 mL Canadian Standard Freeness (CSF) and 470 mL CSF, similar to the paper mill process. Freeness of the final stock was about 360 mL CSF.

Quaternary cationic tapioca starch with a Degree of Substitution (DS) of 2.5% and precipitated calcium carbonate (PCC) with an average particle size of 2.35 µm, 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 a hot plate for 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 during the same day.

The anionic nanosilica sol product, 15% suspension (NP 882) with an average diameter of 2 to 5 nm was acquired from Eka Chemicals Inc.

Polyaluminum chloride (PAC), which is a common anionic trash catcher (ATC), solution containing 10% Al_2O_3 equivalents, was also acquired from Eka Chemicals Inc.

Methods

The furnish was developed using proportionate amounts of the stock (*i.e.*, the original stock with 85% eucalyptus and 15% bleached softwood). To meet 10, 20, and 30% ash contents in the final sheet, several handsheets were made to find out how much PCC loading needed to be added as filler, such that the final sheet would contain the desired ash content. The ash content was measured according to TAPPI T211 om-02 method. As it is very hard to meet the exact amount of 10%, 20%, or 30%, we accepted the negligible amount of ±0.5% as our error in ash content (*e.g.* 20±0.5 or 30±0.5).

Chemicals were added in the following order: Poly aluminum chloride (PAC) at a dosage of 0.05% was added to the fiber furnish. The mixing rate was kept constant at 1000 rpm using a Dynamic Drainage Jar (DDJ) stirrer in a 1-liter beaker. 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. Before papermaking, the pH of the furnish was about 8.5 at 25 ˚C. Without delay, the prepared furnish was transferred to a TAPPI sheet former in which the hand sheets were made according to the TAPPI T205 sp-95 standard. Note that to study the effect of nanosilica – cationic starch combination, all the sheets, even the control samples, contained a constant dosage of PAC as a common anionic trash catcher.

The air permeability of the handsheets was determined using an L&W Air Permeance tester (Lorentzen & Wettre, Sweden). The formation quality of the sheets was measured with an AMBERTEC β-formation tester in which formation was evaluated according to the standard deviation of basis weight at 400 points (the number of points can be adjusted as desired) measured by β-radiation source on top and a β-collector beneath the sheet with basis weight of 60 gr/m^2.

$$\textit{Formation Index (Standard Deviation of Basis Weight)} = \sqrt{\sum^{i=400}(60-xi)^2/(400-1)} \qquad (1)$$

The apparent density was calculated as mass per cubic centimeter, where an electronic scale was used to measure the mass, and the thickness was determined with an L&W Micrometer (Lorentzen & Wettre, Sweden). A Color Touch PC spectrophotometer (Technidyne Corp., USA) was used to determine the brightness and opacity of the handsheets according to ISO 2470 and ISO 2471 standards.

A tensile tester (MTS Inc.) was used to determine the tensile strength according to the SCAN-P 67:93 method. The tear index (Elmendorf method, L&W, Sweden) and internal bonding (Scott-type, L&W, Sweden) were evaluated according to SCAN-P 11:73 and TAPPI T-833 pm-94, respectively.

RESULTS AND DISCUSSION

Physical Properties

Air Permeability

Air permeability of paper can be affected by the size and distribution of the pores created as a result of flocculation in the paper structure. Figure 1 shows that sheets with higher filler addition levels exhibited higher air permeance, while it was reduced when just cationic starch was added to the base furnish. But, the addition of nanosilica, which caused micro-flocculation and affected pore size and distribution, raised air permeance. The trends also showed that the increase in air permeability was more intensive with greater nanosilica dosage. Duffy (1993) confirmed that the microparticle flocculation mechanism increased porosity, which is highly related to air permeability. He added that the improved porosity was responsible for the reduction in energy required to dry the sheet. The increase in sheet porosity was referenced to the fact that the components of the system were able to reflocculate after being dispersed by shear. Nilsson and Carlson (1993) mentioned another indirect effect of nanosilica wet end system on paper strength that normally internal bond was affected by increased porosity through a higher pick up in the size press, such that penetration of size press starch further into the sheet was observed.

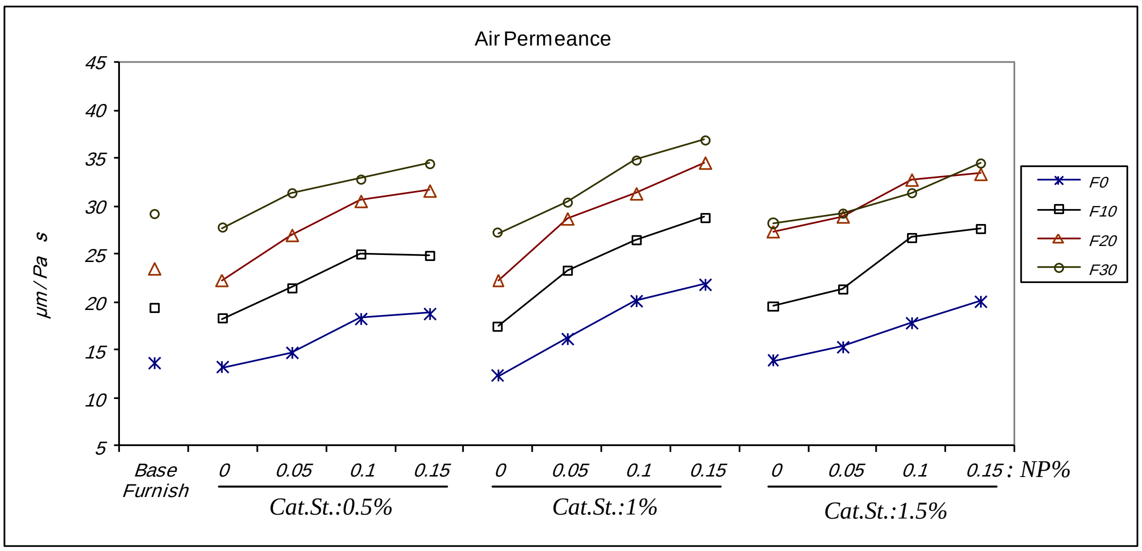

Fig. 1. Influence of nanosilica system on air permeability of fine paper (Bendtsen Method; F: Filler amount (ash content, %), Cat. St.: cationic starch dosage (%), NP: Nanoparticle dosage (%); Dosages based on OD pulp).

Sheet formation

The formation uniformity of a sheet is a significant criterion of fine papers. In Fig. 2, the effects of the microparticle system on formation uniformity of a laboratory hand sheet are compared to the base furnish with no additive. Hence, the figure proposes that flocculation is more severe with more cationic starch and higher nanoparticle dosage levels. Of course, any flocculating mechanism creates some aggregates which, even in the case of tiny dense flocs produced by microparticulating system, adversely affect the formation uniformity compared to the base furnish that contains no additive and is just an ideal blank. But, improvement in retention or drainage and on the other hand formation uniformity determine how efficiently the system acts. Many studies have focused on the efficiency of the system in the case of retention, drainage, and process-related variables (Penniman and Makhonin 1993; Miyanishi 1995; Carr 2004; Khosravani *et al.* 2010; Kim *et al.* 2010).

The microparticle flocculation mechanism differs from conventional flocculation in its ability to reflocculate after shear, and therefore, formation also shows more dependence on paper machine conditions and turbulence. With this system, the bonds can reform immediately after the shear is removed, forming tighter, denser flocs (Duffy 1993). Thus, nowadays, in usual paper machines with high turbulence conditions, the formation improvement due to microflocculation systems seems to be much higher than laboratory results. Figure 2 shows the effect of the nanoparticle system on formation quality in a handsheet former, in which turbulence is minimized. Of course, other retention/drainage programs (such as single polyacrylamide) are expected to induce larger flocs at the same retention or drainage rates (Hubbe 2005). These data will help to compare the formation quality resulted from this wet-end system with the other systems under basically similar laboratory conditions.

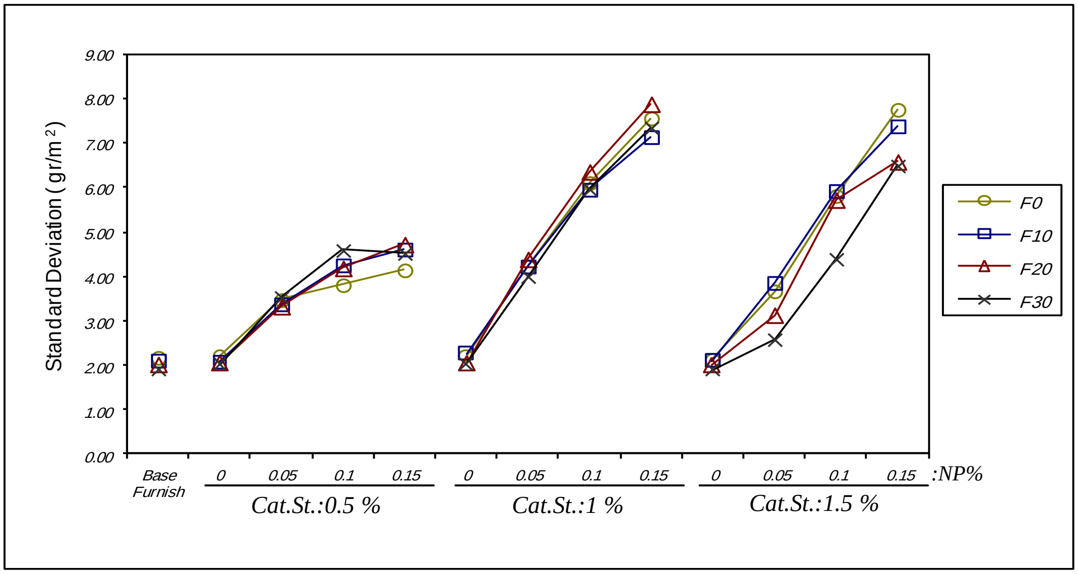

Fig. 2. Influence of nanosilica system on formation uniformity of fine paper (F: Filler amount (ash content,%),Cat. St.: Cationic Starch (%), NP: Nanoparticle dosage (%); Dosages based on OD pulp)

Apparent density

According to theory, paper containing more filler may show lower apparent density, assuming that the filler particles lie between fibers and make paper more bulky and porous (Krogerus 1999). Figure 3 confirms this for the present experimental system. As was discussed earlier, nanoparticles make paper more porous and increase air permeability of the paper. In the same way, nanoparticles also decrease apparent density of the paper. A possible reason is the flocculating effect of nanoparticles that induce some tiny aggregates in paper structure while the neighboring areas lack such dense flocs. The net effect can be a bulky porous structure with a lower apparent density. The proposed schematic figure that can make the idea more tangible is shown as Fig. 4. Studying the air permeation and formation deviation index of the sheets in Fig. 5 also approved this idea.

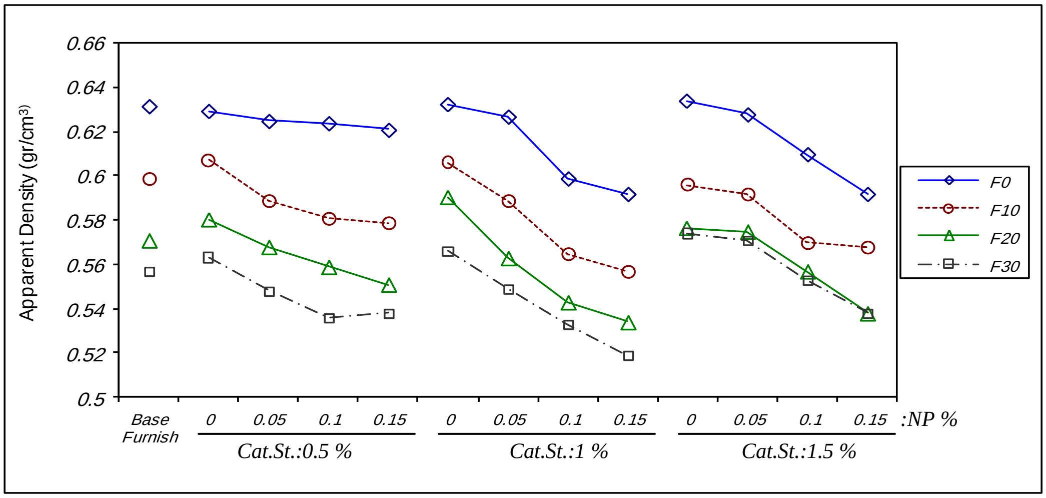

Fig. 3. Influence of nanosilica system on apparent density of fine paper (F: Filler amount (ash content,%),, Cat. St.: cationic starch (%), NP: Nanoparticle dosage (%); Dosages based on oven-dry pulp)

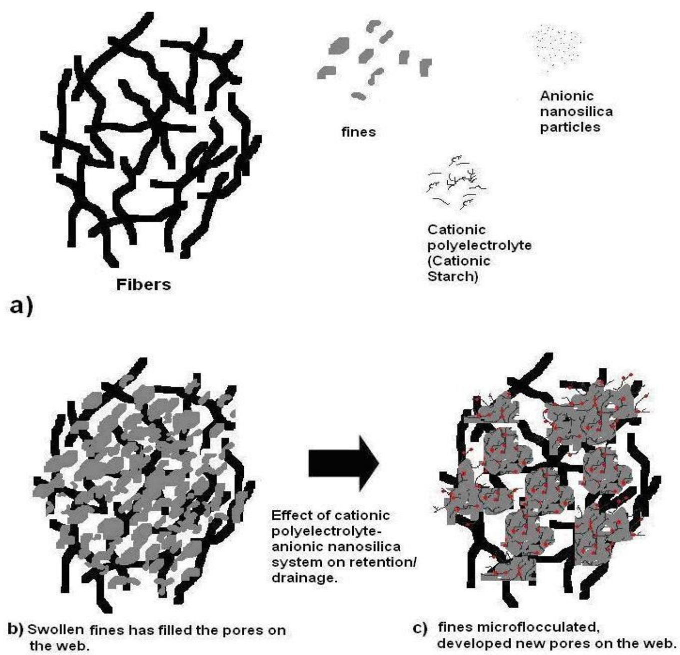

Fig. 4. Schematic representation of cationic polyelectrolyte-fine particles flocculating system (Khosravani *et al*. 2010)

Optical Properties

The use of a greater amount of filler, coupled with the retention of more filler in the paper, can be expected to affect the optical properties. Both opacity and brightness are expected to be relatively high at the higher filler levels. But, when the filler contents were adjusted to a constant level, the nanoparticle by itself did not appear to affect the optical properties directly (Figs. 6 and 7).

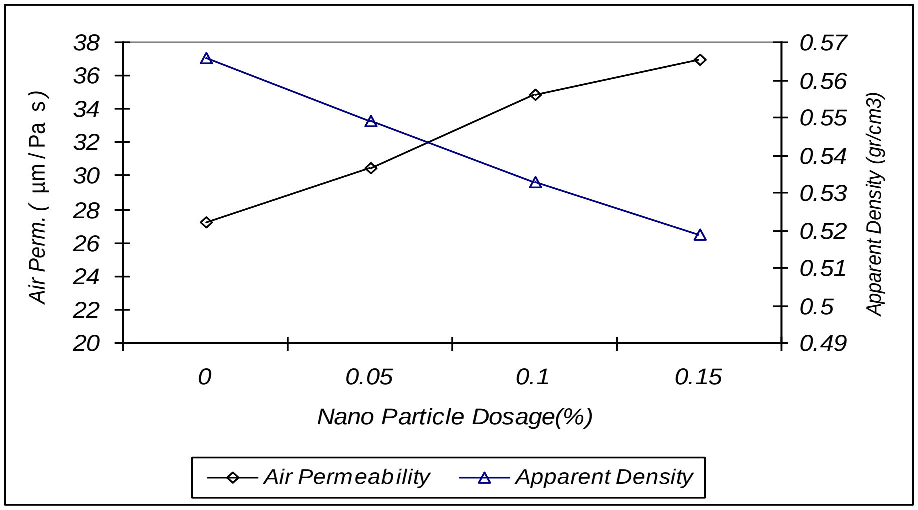

Fig. 5. Influence of nanosilica system on air permeance and apparent density of fine paper (ash content 30%, cationic starch: 1% ; Dosages based on OD pulp)

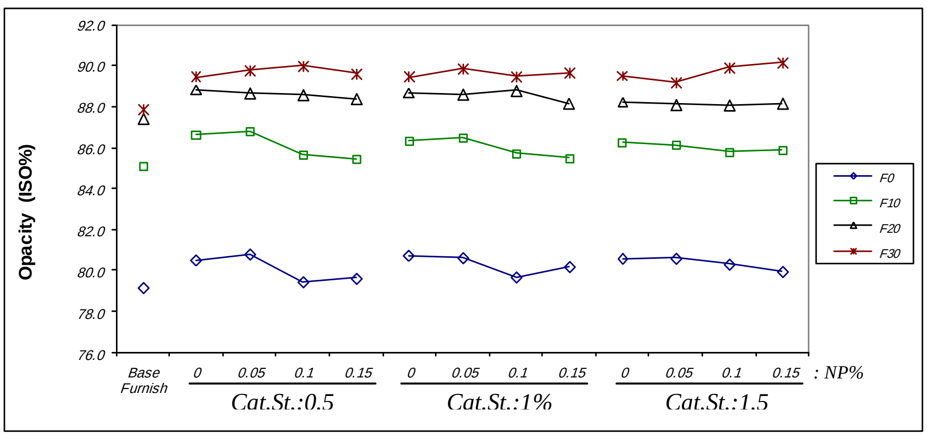

Fig. 6. Influence of nanosilica system on opacity of fine paper at pre-determined constant filler levels (F: Filler amount (ash content, %), Cat. St.: cationic starch (%), NP: Nanoparticle dosage (%); Dosages based on OD pulp)

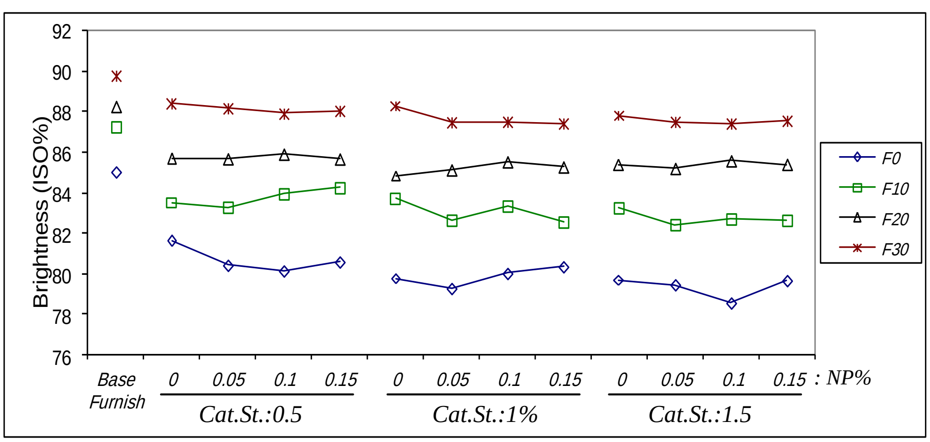

Fig. 7. Influence of nanosilica system on brightness of fine paper at pre-determined constant filler levels (F: Filler amount (ash content, %), Cat. St.: cationic starch (%), NP: Nanoparticle dosage (%); Dosages based on OD pulp)

Opacity of the sheets with the same filler level (series lines) followed no specific trend, as displayed in Fig. 6. The fluctuations may be due to basis weight variances produced as a result of uneven formation. While areas with less basis weight would show less opacity, areas containing dense flocs would seem more opaque.

Opacity of the base furnish also increased with the addition of cationic starch (Fig. 6), while cationic starch reduced the brightness of the base furnish (Fig. 7). As Fig. 7 indicates, the brightness of the furnishes containing more filler (*e.g.* F_{30}: the red line) was less affected by starch addition.

Paper Strength

The main purpose of the strength testing was to evaluate the direct effects of nanoparticles on paper strength. Figure 8 shows the potential effects of this wet-end system on the tensile index of fine paper.

Tensile index of the handsheets with the same filler content can be distinguished by use of the same line color. Generally, these lines are completely distinctive, because filler particles obstruct fiber-to-fiber bonds and significantly reduce the strength of paper (Krogerus 1999). Therefore, the tensile index of sheets with higher filler content obviously appeared as a lower line.

With all filler levels (series lines), when cationic starch was added to the initial furnish, a significant increase in tensile index was observed, although this increase was less pronounced in the case of 30% filler content. This implies that the bonding effect due to cationic starch was offset by the presence of too much filler.

As indicated by Fig. 8, the reduction of tensile index by ten percent increase in filler content (*i.e.* the intervals between: 0, 10, 20, and 30%) was too large to be fully compensated by cationic starch. As was observed, when filler content was increased by ten percent, the tensile index shifted from above the line to the next beneath the line. This reduction could hardly be compensated by any dosage of cationic starch; nevertheless, the smaller filler loadings might be compensated by cationic starch addition.

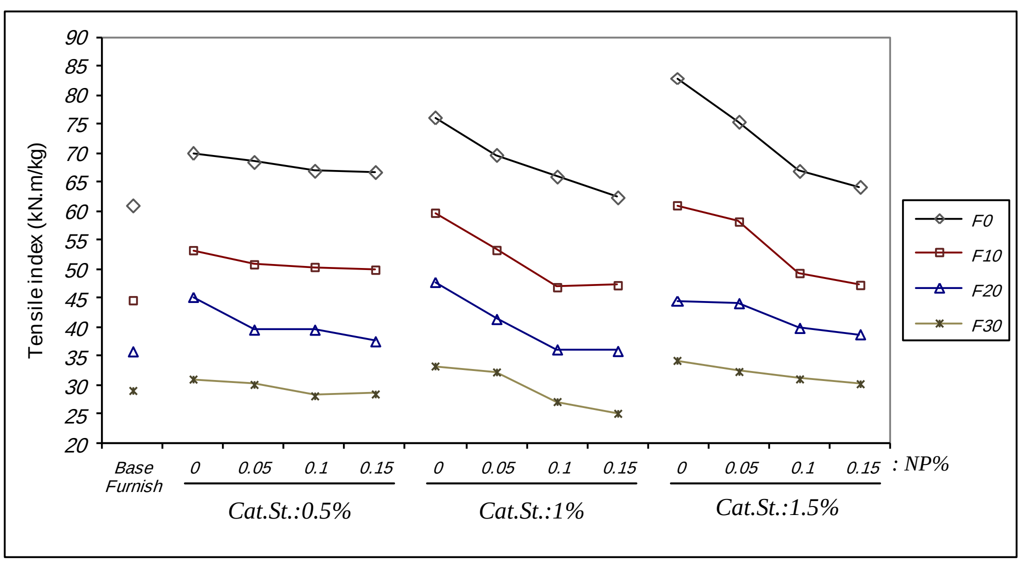

Fig. 8. Influence of nanosilica-cationic starch system on tensile index of fine paper (F: Filler amount (ash content, %), Cat. St.: cationic starch (%), NP: Nanoparticle dosage (%); Dosages based on OD pulp)

When nanoparticles were added with high cationic starch dosages (*i.e.* cationic starch: 1% and 1.5%), the tensile index suffered, but in the case of 0.5% cationic starch, nanosilica addition did not negatively affect the tensile index so much. It is well known that the addition of nanoparticles highly improves retention and drainage by formation of microflocs (Hubbe 2005; Khosravani *et al.* 2010), providing more open channels for water to flow in the spaces between the flocs as the fiber mat is drained. Such open channels can serve as weak areas between the flocs in a sheet of paper. Thus, the loss in tensile index can be attributed to the increased level of flocculation and thus deterioration of formation uniformity (Fig. 9). Kim *et al.* (2010) also reported similar reductions in tensile and burst strength by applying a microparticle system consisting of colloidal silica and cationic polyacrilamide. Note that the performance of this system at 0.5% cationic starch for retention and drainage (Khosravani *et al.* 2010) and also simultaneously, its mild flocculation effects shown above (Fig. 8) are considerable results.

One of the properties that responded very well to starch addition and proficiently indicates the bonding effect of starch is internal bonding, which could even be doubled due to starch addition (Fig. 10).

Figure 10 shows the z-direction bonding effect of starch when it was used in conjunction with colloidal silica. In the case of furnishes that did not contain colloidal silica, cationic starch did as was expected, and starch at all dosage levels increased the internal bonding. Surprisingly, in conjunction with nanoparticles, cationic starch showed even better performance, except at some points with 0% filler content; the corresponding samples probably had too uneven of surfaces to stick to the tape during testing, therefore showed a decrease in internal bonding.

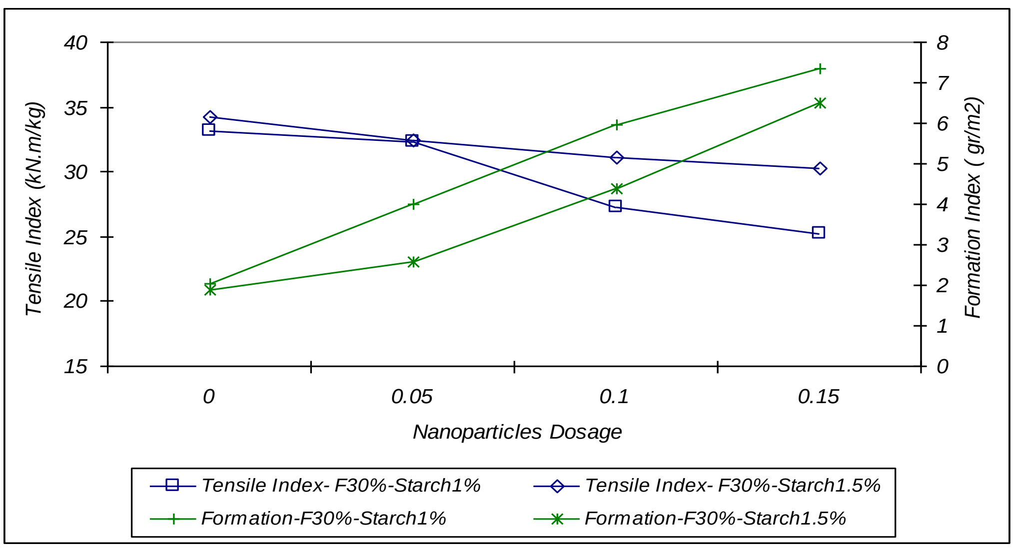

Fig. 9. Influence of nanosilica system on formation and tensile index of fine paper (Ash content: 30%; Dosages based on OD pulp)

There are some interpretations on how nanoparticles boost internal bonding. Some researchers believe that nanoparticles help better starch retention (Aloi and Trksak 1998; Hubbe 2005), therefore it seems that the retained starch is the key factor for internal bonding improvement.

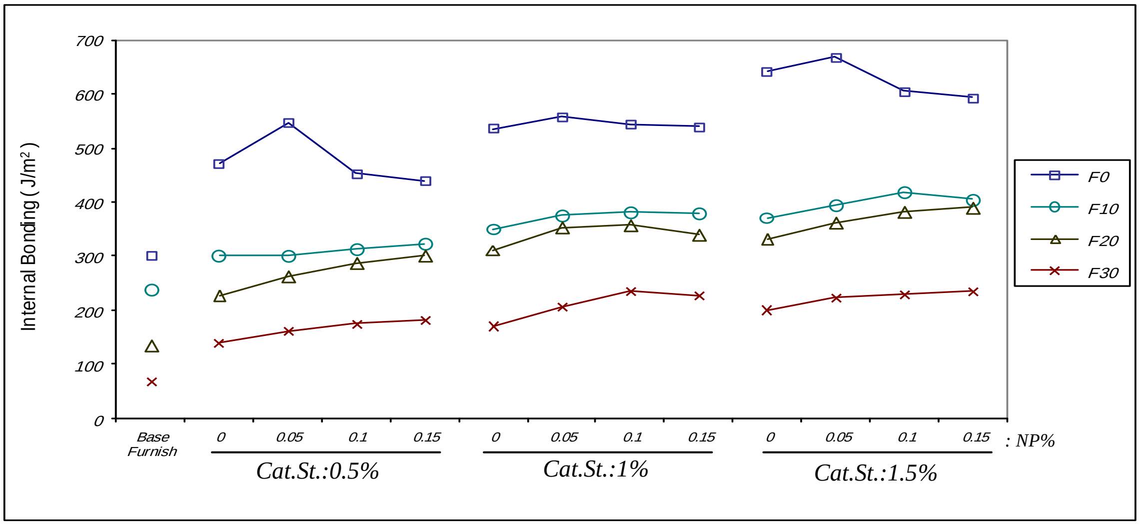

Fig. 10. Influence of nanosilica-cationic starch system on internal boding –Scott type of fine paper (F: Filler amount (ash content, %), Cat. St.: cationic starch (%), NP: Nanoparticle dosage (%); Dosages based on OD pulp).

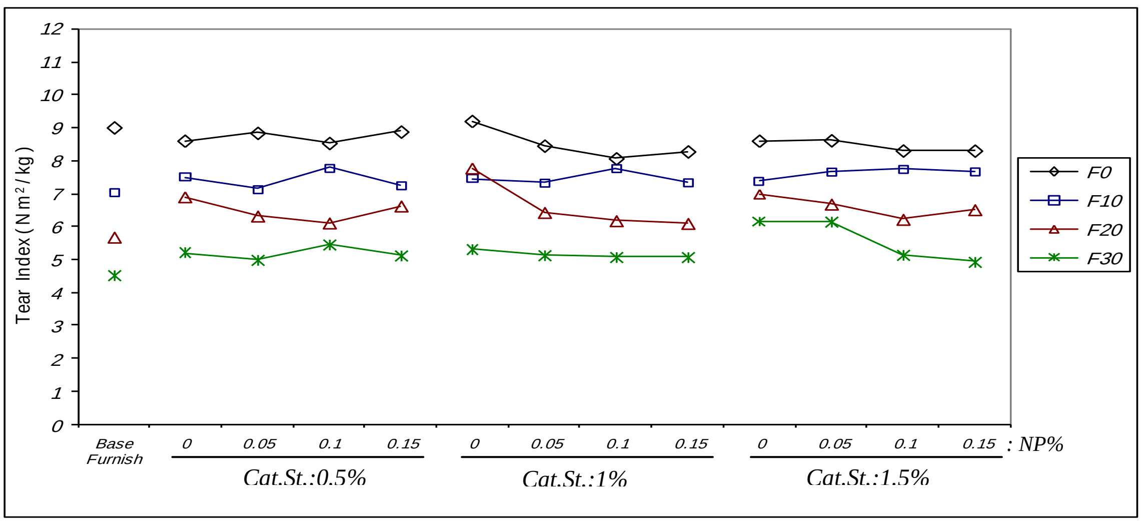

Fig. 11. Influence of nanosilica-cationic starch system on tear index of fine paper (F: Filler amount (ash content, %), Cat. St.: cationic starch (%), NP: Nanoparticle dosage (%); Dosages based on OD pulp).

Tear index is also an important criterion for the evaluation of most fine papers. As Fig. 11 indicates, filler played a significant role to reduce tear index, while only cationic starch improved tear index in the case of filled papers (10%, 20%, and 30% ash content), although this was not true with zero-filled papers. On the other hand, a clear, consistent trend was not observed when nanosilica was also added to the system.

With most wet end systems, in order to achieve higher retention/drainage rates there is an inevitable increase in flocculation that deteriorates formation uniformity and therefore, to some extent, various strength properties. Thus, to evaluate the efficiency of the wet end systems, they should be compared at equal drainage rates and retention efficiencies.

CONCLUSIONS

The direct effects of cationic starch – nanosilica system on paper strength were found to be mostly due to cationic starch as a dry strength agent which, to some extent, provided for the potential use of more filler in fine paper. Nevertheless, in the systems incorporating nanoparticles, microflocs are formed, providing more open channels for water to flow in the spaces between the flocs as the fiber mat is drained. Therefore, nanoparticles make paper more porous, which can cause more starch penetration and uptake during size pressing, which can be proposed as an indirect approach to improve paper strength (Nilsson and Carlson 1993).

Cationic starch and nanoparticles both had positive effects on internal bonding, although the effect of cationic starch was more prominent. Also, tear index should not be neglected. As with more filler, tear index suffered, cationic starch partly compensated for this negative effect with filled papers, but nanoparticles did not seem to have an obvious effect.

Note that in this research, low cationic starch dosages with the nanosilica system seemed to be preferred due to mild flocculation effects on formation and thus achieving acceptable strength properties. Higher starch dosages had too intense of an interaction with nanosilica, which brought about severe flocculation. Meanwhile, these results were obtained under laboratory conditions, and it can be expected that in usual paper machines, especially in new ones with high turbulence conditions, the formation uniformity due to such a microflocculation system will improve much more, even at higher cationic starch dosages.

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