Paper strength factors in systems with nanofibrillated cellulose, cationic starch, colloidal silica, cationic acrylamide copolymer, and hydrodynamic shear

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ABSTRACT: Laboratory paper sheets were formed by first pretreating nanofibrillated cellulose (NFC) with cationic starch at the 5% level by mass. The treated NFC was then added to stock prepared from 100% recycled copy paper. The combined furnish was next optionally treated with a cationic retention aid (cPAM, 0.1%) and then colloidal silica (0.1% or 0.2%). Vacuum dewatering, fine-particle retention, and several paper properties were studied as a function of the colloidal silica level (zero, 1%, and 2%) and at different levels of shear stress applied just before forming the sheets. Dewatering and strength results were generally more favorable when using a medium charge cationic starch (~ 0.03 degree of substitution, DS) to pretreat the NFC rather than a high charge density cationic starch (~ 0.2 DS). In each case, the dewatering was further enhanced by subsequent treatments by cPAM (0.1% on whole furnish solids) and then even more with the final addition of colloidal silica (0.1% and 0.2% levels compared). However, the colloidal silica additions progressively hurt the tensile strength of the paper, especially in the case of the high charge cationic starch and at the higher level of colloidal silica. Though the dewatering performance was favorable, in such cases, the paper strength was not improved compared to paper made without any NFC. The fact that the systems involving cPAM treatment, and especially those involving both cPAM and colloidal silica, tended to reduce the resulting paper's tensile strength supports a mechanism in which the additives result in the clustering of the NFC, possibly in multiparticle bunches. Evidence suggests that such bunches of clustered NFC particles, which are difficult to redisperse even at levels of hydrodynamic shear present in high-speed paper machine systems, are resistant to full integration into the sheet structure as the paper is being formed.

Application: The goal of this work was to determine why adding certain pretreated NFC failed to increase the strength of the resulting paper in laboratory tests. Results suggested that the treated nanocellulose formed clusters that were difficult to redisperse by shear. Treatments that made it possible to maintain suitable drainage levels in the presence of nanocellulose were generally unfavorable for its strength properties.

Papermakers often appear to be striving for contradictory goals. For example, most paper machines employ some form of flocculating chemical to help retain fine particles onto fiber surfaces before the sheet is formed [1-3]. Such retention aid applications not only reduce the amount of fine matter that is sent to the wastewater treatment plant, but they also can reduce the rates of deposit buildup onto the wetted parts of the equipment [4]. Another consequence of retention aid usage, especially at higher dosage levels, can be flocculation of fibers in the suspension, leading to loss of uniformity and often loss of strength in the resulting paper [5]. It has been shown that, to some extent, the problem just described can be managed by judicious usage of hydrodynamic shear, which is achieved by selection of addition points for additives [6,7], in combination with adjustment of chemical dosages or types.

This study concerns another such dilemma that some papermakers may face. In theory, it would be expected that nanofibrillated cellulose (NFC) would be a promising material by which to enhance the interfiber bonding within paper. The term NFC refers to highly fibrillated cellulosic products in which the individual fibrils generally have a thickness of 100 nm or less. Such material also has been called "microfibrillated cellulose," especially in cases where some of the fibrous material exceeds 100 nm in fibril thickness [8]. Various researchers have shown evidence supporting the use of NFC to increase bonding strength of paper [9,10]. A key reason that NFC has not become widely used as a papermaking additive appears to be its strongly negative effect on dewatering rates as the paper is being formed [10].

A strategy to overcome the adverse effect of NFC on drainage rates has been reported [9,11,12]. The first step taken in each of these cited works was to adsorb cationic starch onto the NFC surfaces, followed by agitation and addition to a fiber furnish. Cationic starch was chosen be-

cause it is a well-known dry-strength additive for papermaking [13,14]. Starch products having two different cationic charge densities were considered for the present work. The first, a medium charge cationic starch, was selected because it is representative of the charge density range most often employed in papermaking wet-end applications. The second, referred to as high charge in this study, was selected due to highly promising results that had been obtained with its use when using cationic starch-treated NFC to reinforce bulky paper sheets prepared from unrefined or low-refined kraft fibers [9].

To overcome the adverse effect of NFC on dewatering, the furnish was further treated sequentially, first with cationic acrylamide copolymer (cPAM) and then with colloidal silica (SiO_2) at a favorable ratio of colloidal silica to cationic starch [9,15,16]. The purpose of the cPAM was to serve the role of a retention aid, flocculating the fine particles, such as calcium carbonate ($CaCO_3$) filler, cellulosic fines, and nanocellulose, such that they will be efficiently retained as part of the paper sheet.

In past work, the colloidal silica either was added to the cationic starch-treated NFC before its addition to the fiber furnish [9,15], or it was added to the combined furnish after addition of the cationic starch-treated NFC [17,18]. In the work of Rice et al., which involved some unusually low levels of refining of the fibers, adding the colloidal silica to the cationic starch-treated NFC achieved very high contributions to paper stiffness in addition to favorable rates of dewatering [9]. However, later work reported by Barrios et al. showed a lack of strength benefits when the furnish was treated with cationic-starch-treated NFC followed by colloidal silica addition to the combined furnish [16]. It appeared that the colloidal silica was somehow making the NFC ineffective as a potential strength agent. It has been suggested by Nelson et al. that different results might be expected if similar tests were carried out on a high-speed paper machine, where higher levels of hydrodynamic shear could be expected [16].

The present work, which completes a series of related articles [17-19], emphasizes results of tests using the Wet End Process Simulator (WEPS) device, as well as evaluation of the properties of handsheets prepared with that laboratory equipment. The present work extends the earlier reported findings, especially those of Atree et al. [19]. Finally, a mechanistic proposal is made to explain the results, especially those concerning dewatering and paper strength.

EXPERIMENTAL

Fiber sources and pulp preparation

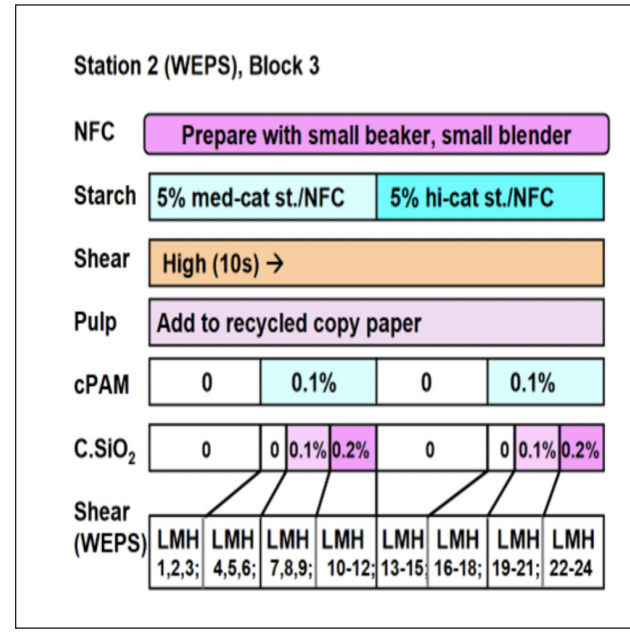
The fiber furnish employed in this work was the same as reported by Hamm et al. [17]. In brief, Boise Aspen recycled multi-use paper (Boise, ID, USA) was redispersed in tap water, which was adjusted to an electrical conductivity of 1 mS/cm at 0.5% solids content with the addition of sodium sulfate.

Chemical preparation

The chemical additives and their preparation were the same as those used in earlier reports in this series [17-19]. Most of the additives and their preparation were described by Hamm et al. [17]. In addition, the colloidal silica was described by Atree et al. [17]. Briefly stated, the two cationic starches were a medium charge density (0.03 degree of substitution, DS) specimen from an anonymous starch company and a high charge density type (0.2 DS, Chargemaster L340) from Grain Processing Corp. (Muscatine, IA, USA). The nanofibrillated cellulose was the default freeze dried version or the TEMPO-oxidized version provided by the University of Maine (Orono, ME, USA). Before use in the present work, it was suspended in water at a 0.5% solids content, with sufficient sodium sulfate having been added to achieve an electrical conductivity of 1000 µS/cm. The cPAM was a conventional dry-bead copolymer of acrylamide and a cationic co-monomer, and it was prepared as 0.1% solids solutions before use. The colloidal silica was the trademarked Fennosil 2180, a structured nanoparticle product from Kemira (Helsinki).

Typical chemical addition sequence

Figure 1 describes the addition sequence employed in this work. A related sequence that did not involving colloidal silica addition had been presented earlier by Hamm et al. [17]. Once again, the sequence of chemical treatments and agitation steps is indicated by the top-to-bottom layout of the figure, corresponding to the progress of the experiment. Again, the horizontal positions in the figure represent different options in the experimental plan.



1. A diagram indicating the sequences of chemical addition and levels of hydrodynamic shear used for each trial (WEPS: wet end process simulator; NFC: nanofibrillated cellulose; cPAM: cationic; SiO_2: colloidal silica; LMH: low-medium-high).

Wet End Process Simulator (WEPS)

Tests using the WEPS device (Sambo Scientific Co.; Seol, Republic of South Korea) followed the same procedures as described by Hamm et al. [17], with the exception that colloidal silica had not been considered in the cited work. In this work, the colloidal silica addition, if present, was always at the 0.1% or 0.2% level, based on furnish solids, and it was always the last chemical additive when used. There were 10 s of agitation provided between each successive addition of a chemical agent. The agitation settings for low, medium, and high shear when using the WEPS were 400, 1000, and 1700 rpm, respectively.

Reported results were obtained following the procedures provided in the instrument manual for the WEPS device. This included using the slopes of the curves for vacuum level as a function of time, which represented the most accurate expression of the dewatering rate. In addition, as recommended in the manual, the final vacuum level at the end of the dewatering cycle was used as an indication of the porosity of the damp fiber mat before it was dried. The formed sheets were removed from the 80-mesh plastic mesh screen supplied with the WEPS. The sheets were pressed and dried according to TAPPI Standard Test Method T 205 "Forming handsheets for physical tests of pulp."

Retention tests

As described earlier [17], tests were carried out with the dynamic drainage/retention jar, i.e., the Britt jar [6,20]. Tests were conducted by agitating the 0.5% solids fiber suspension, to which the specified additives were mixed at specified levels under three conditions of shearing: 400, 600, and 900 rpm. The relative content of unretained material was evaluated by measuring the turbidity of the filtrate using ten replicate measurements for each test. Because, in the absence of retention aid, the filtrate turbidity values exceeded the scale of the device, all filtrate specimens were diluted with water by a factor of ten, and the final results were multiplied by ten.

Flocculation and formation uniformity tests

Tests of the extent of flocculation of the furnish, both before and after chemical additions, were evaluated with the Rank Brothers photometric dispersion analyzer (PDA) device, as described by Hamm et al. [17]. Briefly stated, this method works by using a peristaltic pump to pass the treated 0.5% solids fiber suspension through clear plastic tubing. The root-mean-squared variation in the intensity of the transmitted light is used as an indication of the degree of flocculation. Reported results were from four independent replicate tests.

The degree of nonuniformity in the dry paper was assessed using the Paper PerFect Formation Analyzer from OpTest Equipment Inc. (Hawkesbury, ON, Canada). The C7 channel of data (6.7–13 mm range) was used to represent effects resulting from the assembly or dispersal of fiber flocs.

Tensile, air permeability, and ash content

These tests were carried out using the same equipment as methods described by Hamm et al. [17]. Thus, tensile properties were evaluated with TAPPI Methods T 494 "Tensile properties of paper and paperboard (using constant rate of elongation apparatus)" and T 220 "Physical testing of pulp handsheets." Air permeability was assessed with TAPPI Method T 460 "Air resistance of paper (Gurley method)." Moisture content was determined by first allowing the sheet to equilibrate for at least 20 h under TAPPI standard conditions (23°C ± 1°C and 50% ± 2% relative humidity), weighing them, placing them in a convection oven at 150°C for 30 min, allowing them to cool in a desiccator, and then weighing them again. Filler content was estimated by use of TAPPI Method T 413 "Ash in wood, pulp, paper and paperboard: combustion at 900°C." To apply this test, it was assumed that 100% of the mineral in the handsheets was originally $CaCO_3$ and that the incineration resulted in its quantitative conversion to calcium oxide (CaO).

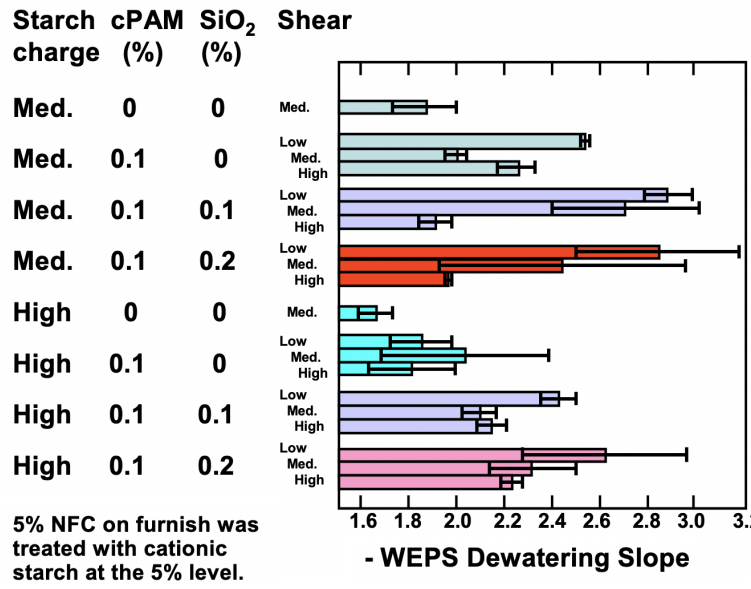
RESULTS

Dewatering rate

Vacuum-induced dewatering rates were determined using the slope of the dewatering line measured by the WEPS device during the handsheet making process. These values are reported automatically by the device. In **Fig. 2**, the dewatering rates are shown for each set of conditions that utilized the default freeze-dried nanofibrillated cellulose (FDNFC) at a 5% level on furnish solids and cationic starch at a 5% level on the FDNFC solids.

To provide background for interpreting the results in Fig. 2, some effects of the different additives on charge demand and zeta potential can be considered. Charge demand measurements had been made corresponding to certain conditions related to Fig. 2. Charge demand test results, as reported by Jones et al. [18], showed that the medium charge and high charge cationic starch solutions had anionic demand values of 50 and 200 μeq/g, respectively. After adding the polymers to the default fiber suspension at the 1% level, the corresponding values had been reduced to 6 and 19 μeq/g, respectively, both indicating a net positive charge. Such results are consistent with the generally negative charge of the default papermaking fibers. In the present work, the net additions of cationic starch, based on a 5% level of NFC added to the furnish and 5% treatment of the NFC by cationic starch, was about 0.25% based on furnish solids. Based on this information, the medium charge cationic starch would not have been enough to fully neutralize the fiber furnish, whereas the high charge cationic starch may have been enough to neutralize the surfaces of the default fiber furnish.

Jones et al. [18] also made measurements of the cationic demand of the cPAM. The polymer was found to have an anionic demand of 1200 μeq/g, which is six times higher



2. Absolute values of the dewatering slopes for each WEPS test. The error bars were determined from the results of two replicate tests.

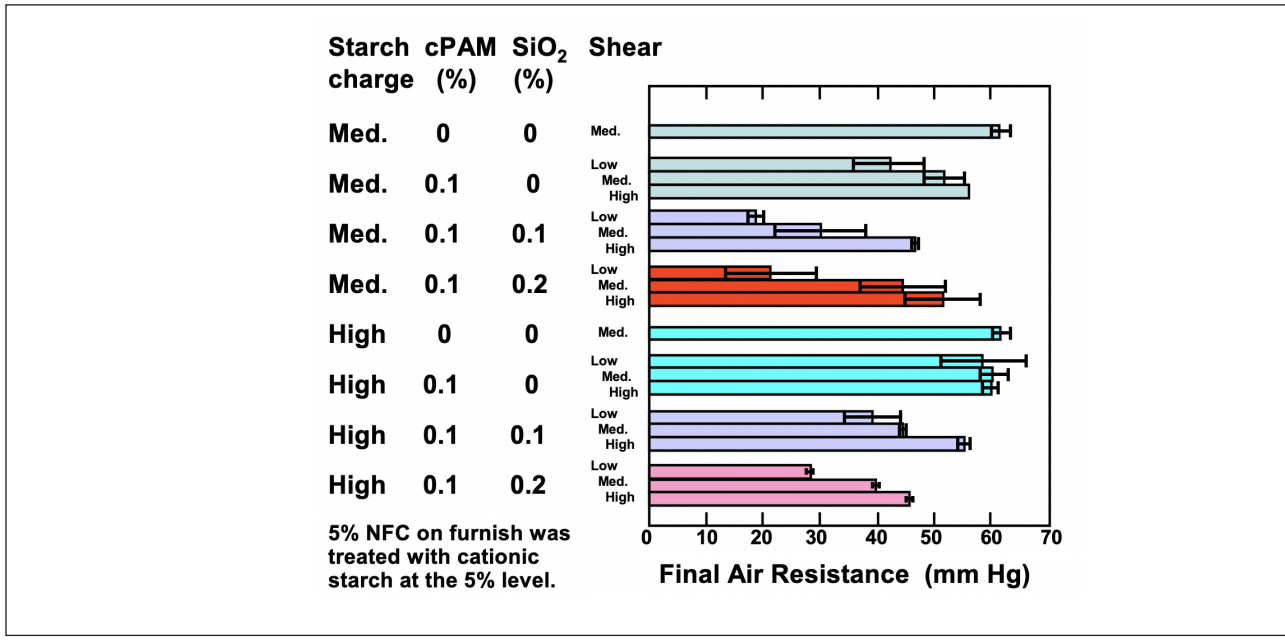
than that of the high charge cationic starch. Though the addition level of cPAM was just 0.1% in conditions where it was used in the current work, it contributed to making the fiber surfaces less negative or more positive. Because the cPAM was added late in the sequence of additives and because of its very high molecular weight (about 3 to 5 million g/mol), it is expected to remain on the outside of fiber surfaces, thus making a relatively large contribution to observed zeta potential values.

Zeta potential measurements reported by Atree et al. [19] can provide some context for conditions represented in Fig. 2, where colloidal silica had been added after the addition of cationic polymers. It had been shown that, after treatment of the furnish with 1% of high charge cationic starch, it was necessary to add colloidal silica at more than the 5% level based on fiber solids to render the zeta potential of the furnish, as a whole, significantly more negative. Since the levels of colloidal silica employed in the current work (0.1% and 0.2% based on solids) were lower than that, one can expect that the changes in zeta potential were low relative to the precision of the measurement method.

The highest dewatering rates occurred when medium charge cationic starch, cPAM, and colloidal silica were all added to the system. The addition of the cationic retention aid without the colloidal silica gave faster vacuum dewatering than the furnish containing only the cationic starch-treated NFC in almost all cases. Colloidal silica addition also favored more rapid dewatering, beyond what was achieved with just the cPAM. However, when medium charge cationic starch was used, there was no additional benefit from using a 0.2% addition level of colloidal silica relative to the 0.1% level.

In systems using the high charge cationic starch to pretreat the NFC (lower part of Fig. 2), the drainage rate was generally slower. The cPAM retention aid addition was not as effective in promoting dewatering compared to the medium charge starch system. Subsequent addition of colloidal silica consistently increased the dewatering rates at both levels of colloidal silica addition. However, under none of the conditions tested were the measured rates of dewatering as high as could be achieved by the best medium cationic starch, cPAM, and colloidal silica systems. There was benefit from the usage of colloidal silica at the 0.2% level when high charge cationic starch was used. It is most likely that the high charge cationic starch shifted the charge balance of the system to the point where more colloidal silica could be added to neutralize that charge. However, it is clear that the use of medium charge cationic starch was much more effective in increasing the dewatering rate than the high charge cationic starch was.

At higher levels of shear, there was a decrease in the drainage rate at almost all levels of cPAM addition and colloidal silica addition. This could be due to the higher shear breaking up flocs of fibers and evenly distributing them in the suspension. When such a suspension is formed into a sheet, the unattached fine matter tends to plug the drainage channels in the web. There also can be a sealing mechanism whereby the fibers block many of the holes in the screen. It is important to note that the trials that utilized high charge cationic starch were less affected by higher levels of shear, whereas the trials that used medium charge cationic starch were greatly affected by increased levels of shear. This indicates that the high charge cationic starch was able to maintain more flocs and prevent the release of fine matter from fiber surfaces.



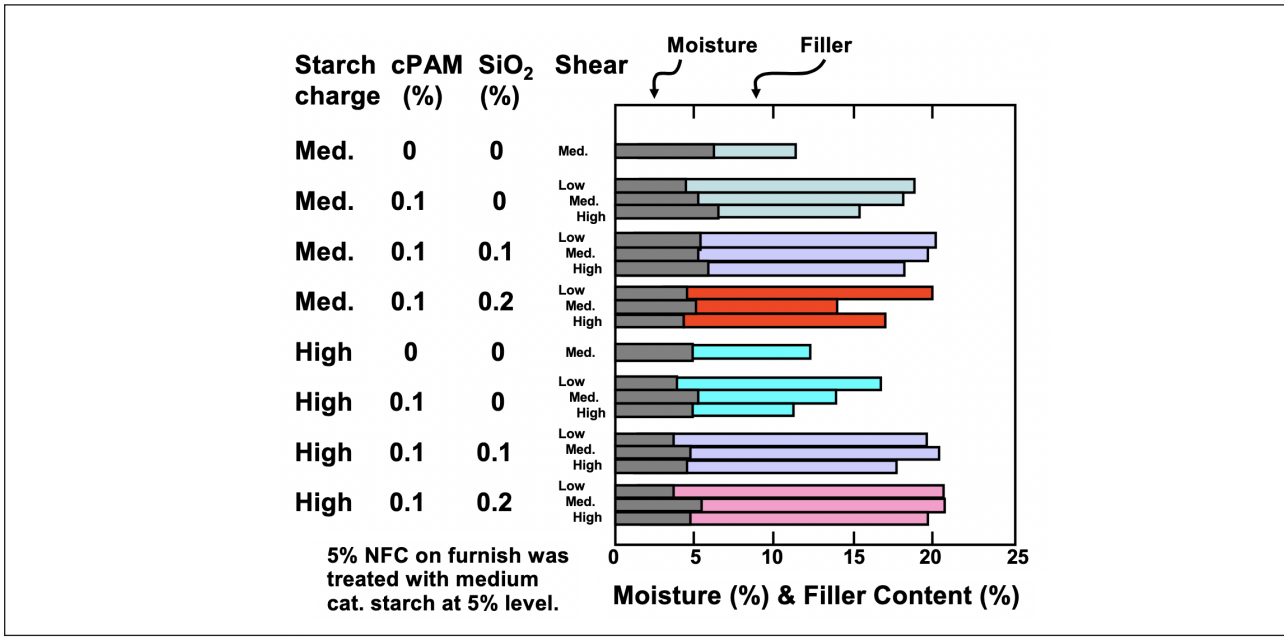
3. Final air resistance for each WEPS test. The error bars were determined from the results of two replicate tests.

Figure 3 shows corresponding results obtained at the end of the vacuum application of the WEPS device. As in the case of the drainage rate data just shown, the resistance to air passage, as indicated by the final vacuum level, can be expected to respond to sealing effects. Such sealing may involve interactions between the cellulosic material and the forming screen. Indeed, results in Fig. 3 showed a negative correlation with those shown in Fig. 2. Such a relationship was also reported by Hamm et al. [17]. In the present case, a regression analysis of the response data shown in these two figures yielded a coefficient of determination (R^2) of 0.8329 that supports the inverse correlation between the two sets of values. The inverse correlation means that the dewatering rate was higher when the final air resistance was lower due to less sealing of the WEPS screen. In Fig. 3, the control trials that did not include any additives other than cationic starch gave some of the highest values of final air resistance. Combinations of cPAM and colloidal silica resulted in lower final air resistance values, which indicates that those combinations kept more drainage channels open. As hydrodynamic shear levels increased, the final air resistance values typically saw an increase for each combination of additives.

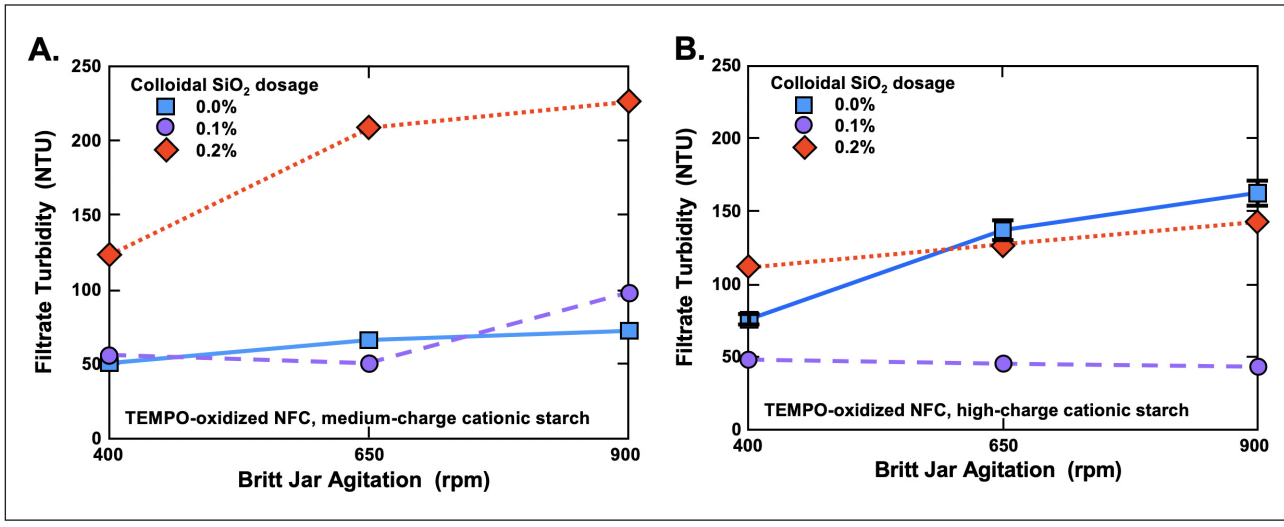
Retention

In **Fig. 4**, the moisture content and filler content of the final paper are shown for each set of conditions that utilized the default FDNFC at a 5% level and cationic starch at a 5% level on the NFC. Large increases in filler content, based on the ash analysis, were observed when cPAM retention aid was used. This highlights how effective the cPAM was at increasing retention efficiency. As the level of hydrodynamic shear was increased, at the same additive levels, there was typically a decrease in the percentage of filler retained in the sheet. In most of the systems, the negative effect on retention efficiency was smaller when moving from low to medium shear compared to moving from medium to high shear, where a larger effect was typically observed. The largest decrease in retention efficiency from increasing hydrodynamic shear came from systems in which the NFC was pretreated with high charge cationic starch and cPAM was added. Systems in which the NFC was pretreated with high charge cationic starch, cPAM was added, and colloidal silica was added exhibited little effect on retention efficiency when hydrodynamic shear was increased. When the NFC was pretreated with medium charge cationic starch, better retention efficiency was achieved when using colloidal silica at the 0.1% level compared to the 0.2% level. This could be attributed to charge flipping, where the charge of the system shifted from slightly positive to negative due to addition of too much anionic colloidal silica. No clear trends could be observed relative to the moisture content levels of each sheet after reaching equilibrium under TAPPI conditions. It was expected that as filler content increased, the moisture content would in turn decrease. An explanation of why this trend was not apparent could be that the NFC and cationic starch are hydrophilic and are retained along with the filler; this then allowed the sheet to absorb more moisture at equilibrium.

Figure 5 shows the results of Britt jar testing in which fine-particle retention was evaluated under varying conditions. TEMPO-oxidized NFC (TONFC) was used in these tests to broaden the extent of the study. The TONFC has a much higher negative charge relative to standard NFC, and the effective surface area is higher than with standard NFC. In Fig. 5A, the TONFC was pretreated with medium charge



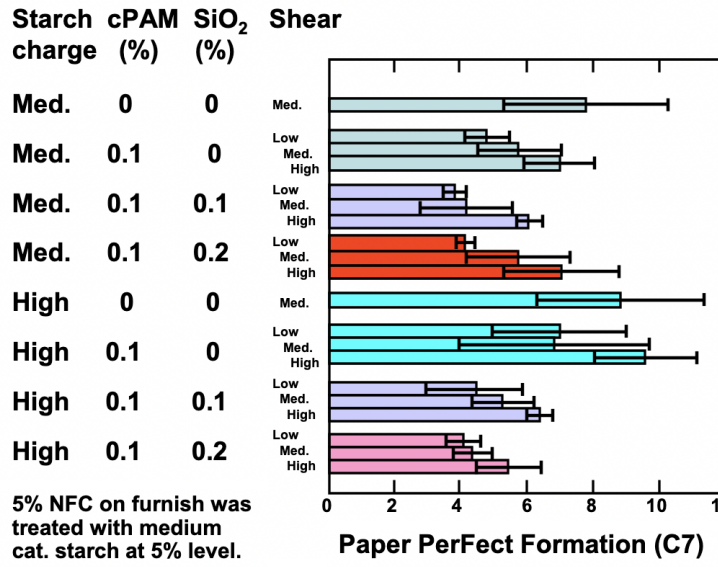
4. Moisture content and filler content, in percentage, for each sheet that was formed on the WEPS. The bars for moisture content and filler content are not cumulative; each go to zero on the x-axis.



5. Filtrate turbidity from Britt jar tests, depending on the addition level of colloidal silica and on the severity of agitation for systems in which TEMPO-oxidized nanobrillated cellulose (TONFC) had been pretreated with cationic starch at the 5% level and added to the default furnish.

cationic starch at the 5% level. Both the agitation level and colloidal silica dosage were varied. Figure 5B followed the same conditions as Fig. 5A, except that the TONFC was pretreated with high charge cationic starch at the 5% level rather than with medium charge cationic starch. In both graphs, the furnish suspension was then treated with cPAM at the 0.1% level on the furnish. Colloidal silica treatment (see legends in Fig. 5A and Fig. 5B) was always the final treatment of the furnish. Turbidity readings were collected 10 times at each condition, with the average of those ten readings shown on each graph.

Two cases can be seen in Fig. 5 where an increase in hydrodynamic shear was able to significantly redisperse the fines relative to the lower shear level. Both cases were most likely caused by excess charge in the system. When medium charge cationic starch was used on the TONFC and a large dosage of colloidal silica was used at the 2% level, there was too much net anionic charge in the system. This caused the charge to flip from positive to excess negative charge and resulted in an unstable suspension that could be affected at higher shear levels. The cPAM was added 10 s before the colloidal silica in each trial, which means, in this case, that the colloidal silica acted as an "anti-retention aid" and was able to affect the already formed polymer



6. Formation uniformity results for sheets formed on the WEPS device, with use of NFC that had been pretreated with cationic starch of the charge densities shown, the cPAM densities shown, and the colloidal silica levels shown, in that order.

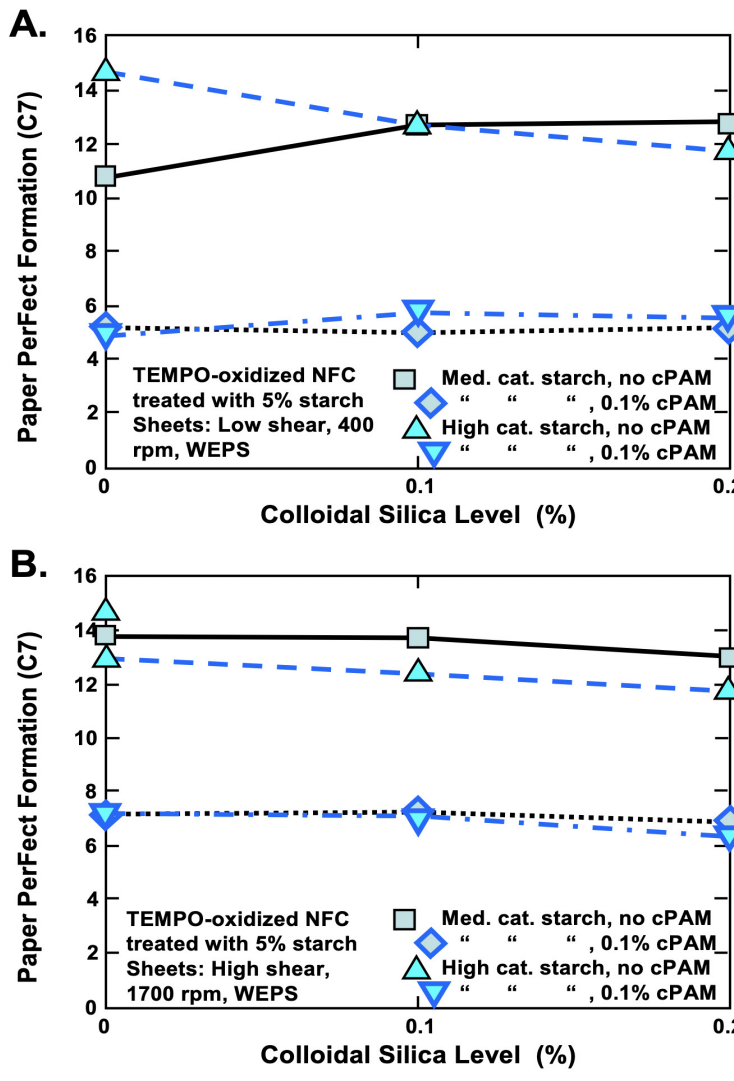
bridges from the cPAM. In the second case, when high charge cationic starch was used followed by cPAM treatment of the furnish, but with no colloidal silica, it was likely an excess positive charge that made the suspension less favorable for retention. The addition of high charge cationic starch in that case shifted the charge balance to very positive, and without any anionic colloidal silica to balance the charge, it led to retention being adversely affected at higher shear levels.

Flocculation and formation uniformity

When using the Paper PerFect device from OpTest to evaluate the uniformity of paper, a higher number means less flocculation and more uniform paper. Thus, as shown in **Fig. 6**, the most uniform paper was associated with systems in which the only additive was 5% NFC that had been treated at the 5% level of cationic starch. Note that two different charge densities of the starch were considered. In the case of the medium charge cationic starch, subsequent addition of cPAM decreased formation uniformity, and a further decrease in uniformity resulted upon subsequent addition of colloidal silica. In the case of the high charge cationic starch, the effect of the cPAM was not as great. A likely explanation for this difference is that the high charge cationic starch had shifted the system to a net cationic charge, which left less opportunity for the cPAM to interact strongly with the solid surfaces and creased polymer bridges. This explanation is supported by the fact that subsequent addition of colloidal silica hurt formation uniformity substantially, and the least uniform sheets were at the higher dosage of colloidal silica.

Effects of differing levels of the final hydrodynamic shear level in the WEPS device relative to the formation uniformity of the paper can be seen by comparing the data within the subgroups of three histogram bars in Fig. 6. In all but one case, there was a progressive improvement in formation uniformity with increasing final shear level. This effect is consistent with the breaking of polymer bridges, leading to better dispersion of the fibers. However, especially in the case of high charge cationic starch (for NFC pretreatment) followed by cPAM and then colloidal silica, even the highest level of shear was unable to restore the paper uniformity to anywhere near its starting condition with just the cationic starch-treated NFC as the only additive. This implies that the fiber flocs formed in that case were too strong to be broken up even by very high levels of shear.

Figure 7 considers the same type of systems as just described, except that the highly negatively charged TONFC was used in place of the default FDNFC, and in addition, only two levels of hydrodynamic shear were compared. The most striking effect shown in these results is a strong worsening of formation uniformity upon addition of the cationic retention aid (cPAM). But unlike the results for the systems with the default NFC, there was no significant change associated with subsequent increased dosages of colloidal silica, as shown on the horizontal axis of Fig. 7. These results suggest that the strongly negative charge of the TEMPO-oxidized NFC shifted the charge balance of the system sufficiently toward the negative side such as to render the colloidal silica ineffective. Again, when comparing Fig. 7A and Fig. 7B, it is apparent that application of a high level of hydrodynamic shear after the cPAM and colloidal silica was only partly able to break up the fiber flocs. About



7. Formation uniformity results for systems similar to those considered in Fig. 6, except that TONFC was used in place of the default freeze-dried NFC.

one-quarter or one-third of the adverse effect of the cPAM treatment on the handsheet uniformity was overcome by the high shear application.

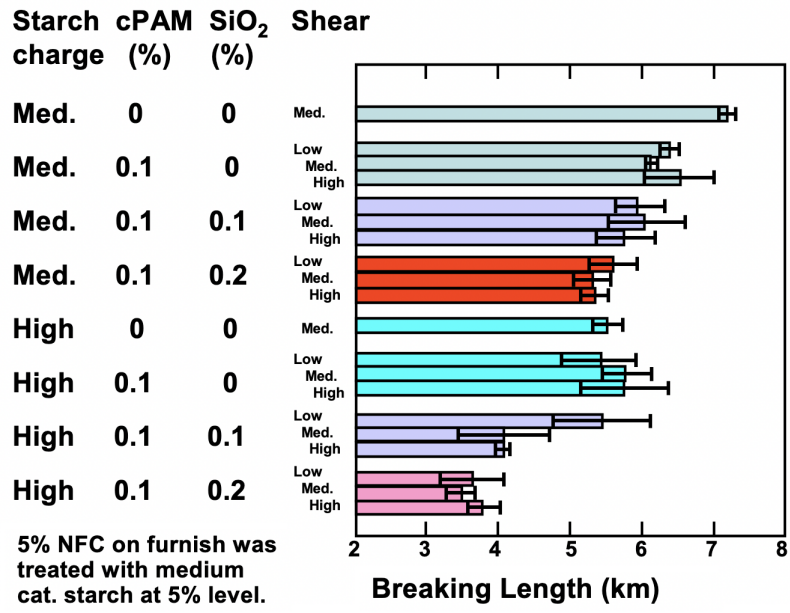
Paper strength properties

The first paper strength property to consider is tensile strength, i.e., the breaking length of strips of paper formed with the WEPS device. By comparing the top half and the bottom half of **Fig. 8**, one can see that sheets formed with the medium charged cationic starch were substantially stronger than those prepared with the high charge cationic starch (as a pretreatment for the default NFC). This difference remained persistent throughout the pattern of changing of dosages of the cPAM and colloidal silica.

In agreement with what was observed for formation uniformity, the cPAM significantly hurt the breaking length only in the case of the medium charge cationic starch. This supports the earlier statement that in the case of the high charge starch pretreatment of the NFC, the system had become sufficiently cationic so as to render the cPAM ineffective as a flocculant.

Subsequent addition of colloidal silica further decreased the paper strength, and the effect was especially strong in systems where the NFC had been pretreated with the high charge cationic starch. The latter effect suggests a very strong interaction between the colloidal silica and the cationically treated cellulosic material, leading to strong flocculation. It is well known that a nonuniform sheet of paper tends to be a weak sheet of paper [5].

Something in Fig. 8 that had not been anticipated was the fact that the very large changes in the level of the final hydrodynamic shear applied during the WEPS experiments did not result in statistically significant differences in tensile strength under any of the conditions investigated. This was



8. Breaking length (tensile strength) results for paper sheets prepared with the WEPS device.

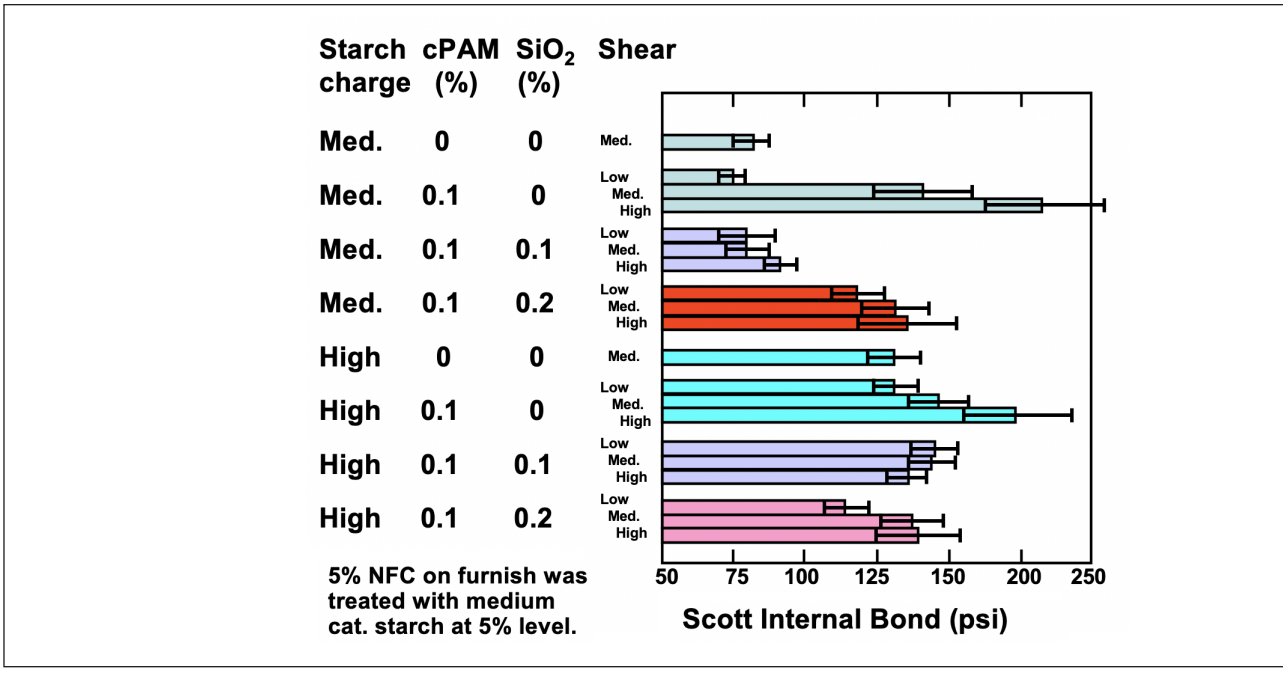
despite the fact that it had been shown earlier that increasing shear had two effects that ordinarily would be expected to make the sheets stronger. Thus, as had been shown in Fig. 6, increasing levels of hydrodynamic shear before sheet formation made the paper more uniform in almost every condition considered. In addition, as had been shown in Fig. 4, especially in the case of the medium charge cationic starch pretreatment of the NFC, higher hydrodynamic shear usually decreased the retention of filler in the paper. One way to explain this situation is to assume that the retention of filler and the retention of NFC were highly correlated. Since the filler would be expected to hurt paper strength and NFC ordinarily has been regarded as a bonding agent, the effects of different retained amounts might possibly balance each other out. Such a line of reasoning, however, neglects the possibility that the effect of retained NFC may also depend on whether it is clumped up or stretched out, etc. Notably, earlier work by Jones et al. [18] showed that that cationic starch treatment induced clumping of NFC, and even the intense shearing in a blender was only partly effective in reversing such effects. Subsequent results reported by Atree et al. [19] showed more effective redispersal of cationic starch-treated NFC after subsequent treatment with colloidal silica, but such results are not necessarily representative of realistic papermaking conditions. For instance, the shear intensity imparted by a kitchen blender appears to be about an order of magnitude larger than that of the maximum shear level generated by the WEPS device.

Due to the importance of paper strength attributes, as well as some not-yet-explained features of the results just shown, further strength-related tests were carried out. Thus, **Fig. 9** shows results of the Scott bond test as measured using TAPPI Method T 569 om-22 "Internal bond strength (Scott type)." This test was chosen because its results usually are less affected by differences in formation uniformity. It provides information about how much energy is required to delaminate the paper.

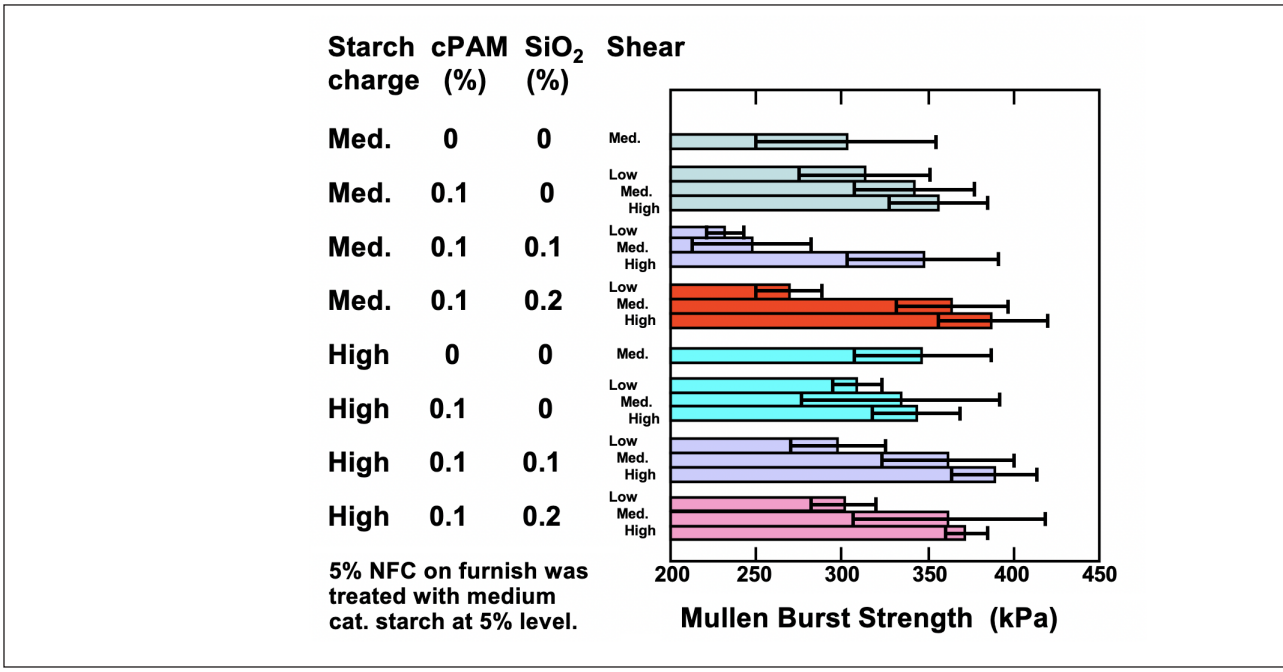
One of the surprising findings for Scott bond was that the effects of the two charge densities of cationic starch were essentially reversed in comparison to the tensile strength results. The default pretreatment of the NFC with medium charge cationic starch gave low Scott bond strength, though the strength was surprisingly increased by subsequent treatment with cPAM and then by increased levels of shearing. A likely explanation for the reversal of some of the trends may be that flocculation of the fibers within paper will tend to increase the proportion of fibers oriented in the thickness direction. Thus, it is reasonable to expect that combinations of additives that tend to flocculate the fibers may increase the Scott bond results, whereas they would be expected to decrease the tensile breaking length.

Effects of hydrodynamic shear were mixed relative to the results of the Scott bond tests. Colloidal silica hurt the strength of sheets prepared with medium charge cationic starch pretreatment of the NFC, followed by cPAM. However, in the case of the high charge density cationic starch pretreatment of the NFC, the colloidal silica addition did not have large effects.

Mullen burst tests results are often correlated with tensile strength results, though the mechanism of breakage is believed to be more complex. Paper that combines an ability to be elongated, in addition to high tensile strength, can



9. Scott bond test results for the same paper specimens considered in the previous figure.

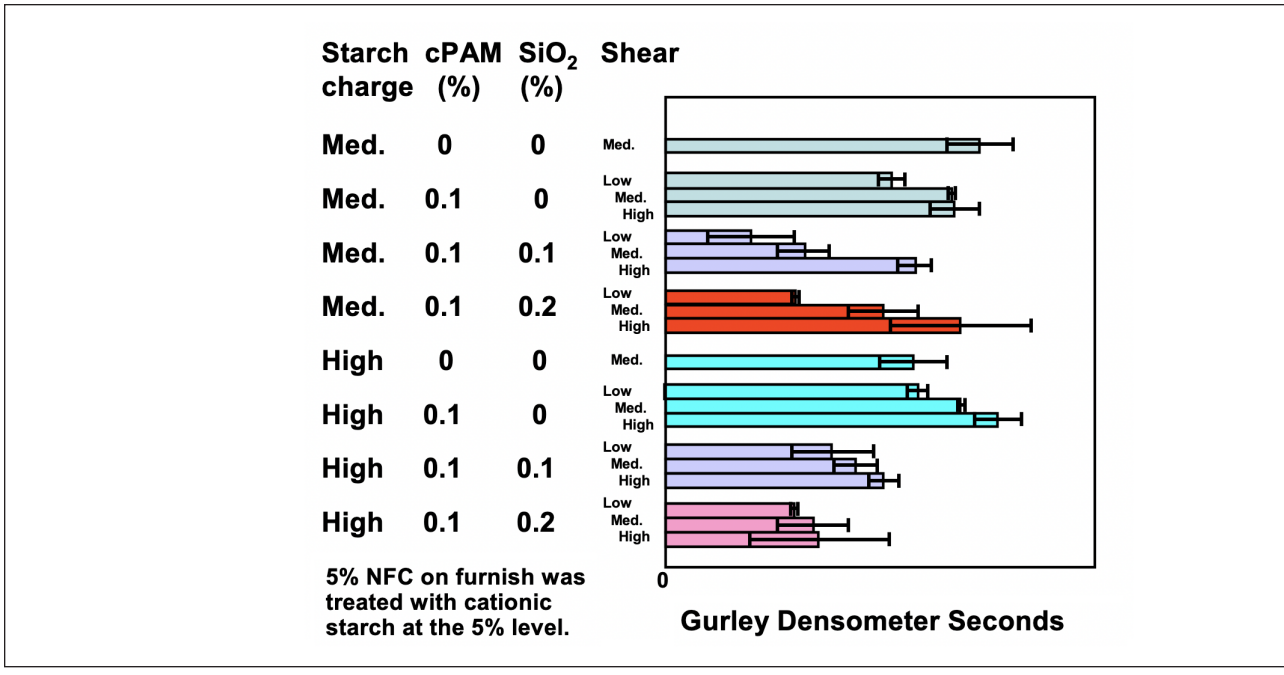


10. Mullen burst strength results for the same specimens considered in the previous two figures.

be expected to give high burst numbers. It can be noted in **Fig. 10** that in most cases the burst strength increased with increasing final shearing of the slurry before sheet formation. This was especially true for the system where the NFC had been pretreated with the medium charge cationic starch, then with addition of cPAM to the furnish, followed by colloidal silica at the lower dosage. The higher dosage of colloidal silica gave high burst strength when followed by medium or high levels of shear.

Sheet porosity (dry)

As a final source of information for the purpose of understanding the overall findings of this work, **Fig. 11** shows the results of Gurley densometer tests, which measure the time required for 100 cm^3 of air to permeate through the sheet under pressure. Earlier it had been shown that the presence of NFC in paper had a major effect of increasing the air permeation time [17]. However, in the cited work, it was shown that flocculation by cPAM made the paper more



11. Gurley densometer seconds results for the same specimens considered in the previous three figures.

porous, reducing the effect of the NFC on that property. The same trend is shown in Fig. 11 for systems that were prepared with medium charge cationic starch pretreatment of the NFC, then cPAM, and then colloidal silica. The results are consistent with this combination of additives being able to form clusters of the pretreated NFC, such that it then had less ability to occlude the pores in the paper. But subsequent application of hydrodynamic shear appeared to uncoil the pretreated NFC, even after colloidal silica treatment, such that it could again act as a partial sealant for air. For systems in which the NFC had been pretreated with high charge cationic starch, then treated with cPAM, and then colloidal silica, the subsequent application of high shear did not have a statistically significant effect. This finding confirms an earlier statement to the effect that the strength of polyelectrolyte complexing interactions in systems containing high charge cationic starch and colloidal silica were sufficiently strong that the effects could not be reversed, even by intense shearing.

DISCUSSION

Up to just before the start of the 19th century, all paper was made by hand [21]. In Europe, including England, as each sheet was couched from the screen using a felt, it was neatly placed at the top of a pile (called a "post") of previously formed sheets. Then, the post of sheets was placed in a screw press, which was used to squeeze out much of the water. Then sections of the post, comprised of several sheets each, were hung in an attic to dry. Even though the sheets had been pressed and dried in contact, still it was possible to separate the sheets in this routine papermaking operation. This ease of separation suggests that there was a lack of interleaving between fibers and/or fibrils associated with each of the adjacent separately formed sheets. By contrast, in a well-formed paper sheet, the fibers are interleaved in a way that can be compared to one's two hands when placed together such that the fingers intertwine.

It is proposed here that a related mechanism may be responsible for cases in which cationic starch-treated NFC present in paper failed to contribute to increased strength. Results of the present work, in combination with articles in this series [17-19], provide evidence to support a hypothesis that, depending on the details, the cationic starch-treated NFC, especially after treatment with cPAM and sometimes with subsequent treatment with colloidal silica, becomes clumped up, and it may fail to become redispersed as elongated individual fibrillar structures even after application of hydrodynamic shear. It is proposed that similar to the wet handmade paper sheets that had been pressed together and dried as posts, the balled-up NFC-rich structures failed to become well integrated with the adjacent fibers in the paper as it was being pressed and dried. McKenzie had theorized that the ordinary practice of papermaking using refined cellulosic fibers results in interdigitization of the fibrils on adjacent fiber surfaces as a means to achieve strong interfiber bonding [22]. In this context, it makes sense that a balled-up NFC structure, possibly lacking in fibrils directed outwards, might not be well suited to integration on a nano scale with adjacent cellulosic material, because the ends of the fibrils are not being exposed.

A key finding of this work was that, depending on the specific formulation, the effects attributed to the clumping of the NFC were unable to be reversed, at least not completely. In particular, when high charge density cationic

starch was used to pretreat the NFC, followed by treatment of the furnish with cPAM and colloidal silica, outcomes such as paper strength were not fixable by applying hydrodynamic shear. These findings are in line with the concept suggested by Jones et al. [16], who found evidence of multiparticle NFC clusters that were not easy to redisperse by shear. Interestingly, micrographs shown by Atree et al. [19] appeared to show greater redispersion of cationic starch-pretreated NFC that had been subsequently treated by colloidal silica. Such results are consistent with the following: (a) a relatively weak charge interaction between the medium charge cationic starch and the colloidal silica, and (b) the very intense shearing provided by a kitchen blender. In the present work, low tensile strength was observed, especially in systems with not only cationic starch-treated NFC, but also cPAM and colloidal silica. The stronger charge interaction between the negatively charged colloidal silica and the cPAM (which has a much greater positive charge density than the medium charge starch [18]) could also contribute to some of the low tensile strength found in the present work.

As an overall general finding, the results of the present work can be envisioned as a validation of practices developed over centuries of traditional papermaking, first in China and then elsewhere in Asia, the Islamic world, Italy, the Netherlands, and ultimately throughout the world [21]. A notable feature of handcraft papermaking traditions is that none of them involved the use of nanofibrillated cellulose. It seems likely that any handcrafters who had experimented with very highly refined cellulosic fibers would have discovered a relatively poor return on their investment in effort, slow rates of dewatering, and poor retention of the extensively overbeaten fibers. Modern papermakers have the option of trying to cheat the system by employing such additives as cationic starch, cPAM, and colloidal silica, aiming to overcome the problems with respect to dewatering and retention. But it appears that gains made with respect to dewatering in the presence of nanocellulose may merely clump up that nanomaterial, leading to unfavorable strength results. In other words, one cannot always have one's cake and eat it too.

While the discussion presented here may be one way to account for the present findings, other mechanisms also can be considered further in future work. For instance, recent work has shown that cationic precipitated $CaCO_3$, when added to a suspension of NFC, was able to promote dewatering, but that the combination resulted in lower-strength composites compared to when anionic $CaCO_3$ was employed [23]. The cited authors proposed that the use of cationic $CaCO_3$ may have hindered hydrogen bonding between solids within the composite. Another possibility is that the electrostatic interactions between polyelectrolytes can be strong enough to create imperfections within the resulting structure of composite material [24,25]. Defects within a composite structure can then serve as weak points, leading to a reduced ability to sustain various stresses applied during testing.

Another possible explanation for relatively low strength results when paper structures are treated with bonding agents or the fibers are subjected to increased mechanical refining is a reduction in the tolerance of the structure to elongation [26-28]. In other words, increased interfiber bonding sometimes leads to embrittlement. However, such effects are typically observed when evaluating the energy required to tear paper [28], and no such measurements were included in the present work.

A recognized deficiency of the present work is that there was no effort to determine global optimum conditions of the independent variables. The chosen combinations of variables such as the starch charge density, whether or not the cationic retention aid was used, and two optional dosages of colloidal silica are most likely not going to have achieved the most advantageous results, except as a result of a lucky chance. The emphasis here was on revealing information about likely mechanisms by which such variables affect practical results, such as drainage rates and strength. If follows that people who are interested in following up with some aspects of this work will at some point need to do some fine-tuning, either by means of designed experiments or by a process of improvements involving production trials during the manufacturing of paper. Also, future work might emphasize options that do not entail pretreatment of the nanocellulose with a cationic polymer.

CONCLUSIONS

Results of laboratory tests using a dynamic sheet forming method, 100% recycled copy paper furnish, cationic starch-pretreated NFC, cPAM, and colloidal silica were able to shed light on some nanoscale mechanisms that help to explain the outcomes in terms of papermaking. Higher tensile strength results were achieved when the NFC was pretreated with a medium charge density (~ 0.03 DS) cationic starch. The lower strength resulting from use of the high charge cationic starch (~ 0.2 DS) is consistent with an expected stronger level of flocculation, especially following treatment with colloidal silica. Once NFC had been treated with either of the cationic starches, followed by addition to the default furnish and treatments with cPAM and colloidal silica, the NFC behaved as if it were a separate phase of material that did not integrate well with the adjacent fibers during the formation of the paper, resulting in low tensile strength. Another key finding is that the tensile strength of the paper showed no significant influence on very large changes in hydrodynamic shear just before paper formation. The overall results of this work suggest that various chemical treatments, including cPAM and colloidal silica, tended to agglomerate the cationic starch-pretreated NFC into clumps in such a way that it was not readily incorporated into the structure of the paper. **TJ**

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LITERATURE CITED

1. Krogerus, B., "Papermaking additives," in *Papermaking Science and Technology: Papermaking Chemistry*, Book 4, Gummerus Oy, Jyväskylä, Finland, 2007, pp. 56-121.
2. Hubbe, M.A., Nanko, H., and McNeal, M.R., *BioResources* 4(2): 850(2009). https://doi.org/10.15376/biores.4.2.850-906.
3. Nokelainen, J., Rantala, T., and Kauppinen, L., "Control and optimization of retention," in *Advances in Papermaking Wet End Chemistry Application Technologies* (M.A. Hubbe and S. Rosencrance, Eds.), TAPPI Press, Peachtree Corners, GA, USA, 2018, Chap. 7, p. 153.
4. Sutman, F. and Nelson, M., "Organic contaminant control: Pitch and stickies," in *Process Chemicals for Papermaking* (M.A. Hubbe and S. Rosencrance, Eds.), TAPPI Press, Peachtree Corners, GA, USA, 2022, Chap. 6, p. 151.
5. Linhart, F., Horn, D., Eisenlauer, J., et al., *Wochenbl. Papierfabr.* 115(8): 331(1987).
6. Britt, K.W. and Unbehend, J.E., *Tappi* 59(2): 67(1976).
7. Hubbe, M.A., and Wang, F., *TAPPI J.* 1(1): 28(2002).
8. Klemm, D., Kramer, F., Moritz, S., et al., *Angew. Chem., Int. Ed.* 50(24): 5438(2011). https://doi.org/10.1002/anie.201001273.
9. Rice, M.C., Pal, L., Gonzalez, R., et al., *TAPPI J.* 17(7): 395(2018). https://doi.org/10.32964/TJ17.07.395.

ABOUT THE AUTHORS

We conducted this study because questions about paper strength had not yet been fully considered, especially in response to colloidal silica addition to systems containing cationic starch-treated nanocellulose and cationic retention aid. That critical step was completed in the present work.

This work is closely related to papers published in *TAPPI Journal* by Hamm et al. [17], Jones et al. [18], and Atree et al. [19]. These three papers considered related issues of drainage, wet-end operations, and paper properties, but they did not consider effects of colloidal silica addition on strength. This article did.

Many papers have failed to address critical concerns about poor drainage and unpredictable strength results when using nanocellulose in paper. This work makes it possible to explain such results.

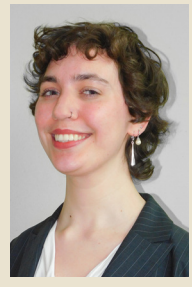
We discovered that a team of undergraduate students, with use of some specialized equipment, can find evidence for fresh explanations about effects of nanocellulose, cationic starch, cationic acrylamide, and colloidal silica on wet-end operations. A finding of particular interest was that, though some other mechanisms might also be at work, our evidence seems to indicate that in the presence of papermaking additives, nanocellulose can form "balls" of tangled material that lose its ability to contribute to paper's dry strength.

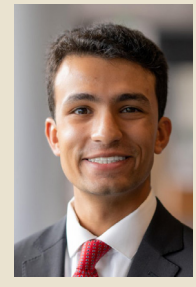
The next steps in this research will need to be carried out in research laboratories and not in mills yet. If nanocellulose is to be added at the wet end of paper machines, some additional laboratory work, including fresh strategies for combining the additives, appears to be needed.

Certain mechanistic questions arose during the progress of this research. For instance, we want to know whether nanocellulose is retained onto fiber surfaces before formation of the paper. Suitable experiments might be considered during the Fall 2025 or 2026 sessions of the Wet End & Polymer Chemistry course at North Carolina State University.

Kozel, Jones, Atree, and Hamm are undergraduates in the Paper Science and Engineering program of the Department of Forest Biomaterials in the College of Natural Resources at North Carolina State University (NCSU), Raleigh, NC, USA, where Hubbe is professor. Email Hubbe at hubbe@ncsu.edu.


Kozel


Jones


Atree


Hamm


Hubbe

10. Salas, C., Hubbe, M., and Rojas, O.J. "Nanocellulose applications in papermaking," in *Production of Materials from Sustainable Biomass Resources* (Z. Fang, R.L. Smith, Jr., and X.-F. Tian, Eds.), Biofuels and Biorefineries, Vol. 9, Springer, New York, 2019, Chap. 3, pp. 61-96. https://doi.org/10.1007/978-981-13-3768-0_3.
11. Hubbe, M.A., *Appita J.* 72(2): 82(2019).
12. Garland, L.J., Leib, B.D., Barrios, N.A., et al., *TAPPI J.* 21(10): 563(2022). https://doi.org/10.32964/TJ21.10.563.
13. Harvey, R.D., Klem, R.E., Bale, M., et al., "Cationic starches in papermaking applications," *1979 Retention and Drainage Seminar Notes*, TAPPI Press, Atlanta, 1979, pp. 39-46.
14. Sharma, M., Aguado, R., Murtinho, D., et al., *Int. J. Biol. Macromol.* 162: 578(2020). https://doi.org/10.1016/j.ijbiomac.2020.06.131.
15. Leib, B.D., Garland, L.J., Barrios, N.A., et al., *TAPPI J.* 21(10): 572(2022). https://doi.org/10.32964/TJ21.10.572.
16. Barrios, N.A., Garland, L.J., Leib, B.D., et al., *TAPPI J.* 22(2): 107(2023). https://doi.org/10.32964/TJ22.2.107.
17. Hamm, K.V., Kozel, D.J., Jones, L.A., et al., *TAPPI J.* 23(9): 477(2024). https://doi.org/10.32964/TJ23.9.477.
18. Jones, L.A., Atree, V.S., Hamm, K.V., et al., *TAPPI J.* 23(9): 491(2024). https://doi.org/10.32964/TJ23.9.491.
19. Atree, V.S., Hamm, K.V., Kozel, D.J., et al., *TAPPI J.* 24(5): 241(2025). https://doi.org/10.32964/TJ24.5.241.
20. Britt, K.W., *Tappi* 56(10): 46(1973).
21. Hunter, D., *Papermaking. The History of and Technique of an Ancient Craft*, Dover, New York.
22. McKenzie, A.W., *Appita* 37(7): 580(1984).

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23. Rao, P.D., Bousfield, D.W., and Tripp, C.P., *Cellulose* 29(9): 4919(2022). https://doi.org/10.1007/s10570-022-04592-9.
24. Wang, Y., Stedronsky, E., and Regen, S.L., *J. Am. Chem. Soc.* 130(49): 16510(2008). https://doi.org/10.1021/ja808135e.
25. Wang, L.M., Wang, L., and Su, Z.H., *Soft Matter* 7(10): 4851(2011). https://doi.org/10.1039/c1sm05158j.
26. Zauscher, S., Caulfield, D.F., and Nissan, A.H., *TAPPI J.* 79(12): 178(1996).
27. Zauscher, S., Caulfield, D.F., and Nissan, A.H., *TAPPI J.* 80(1): 214(1997).
28. Kjellgren, H. and Engström, G., *TAPPI J.* 4(8): 7(2005).

