Effects of hydrodynamic shear during formation of paper sheets with the addition of nanofibrillated cellulose, cationic starch, and cationic retention aid

KENSLEY V. HAMM, DANIEL J. KOZEL, LUCY A. JONES, VARUN S. ATREE, JEONG-YONG RYU, AND MARTIN A. HUBBE

ABSTRACT: Laboratory tests were conducted to evaluate effects of hydrodynamic shear levels on papermaking process variables and paper handsheet properties. The furnish was from 100% recycled copy paper, to which was added nanofibrillated cellulose (NFC) at the 5% level following its optional pretreatment with cationic starch. A cationic copolymer of acrylamide (cPAM) was used as the retention aid. Different levels of hydrodynamic shear were applied both after mixing the NFC with the cationic starch (pre-shearing) or after all the furnish components had been combined (final shearing). The presence or absence of pre-shearing was found to have little effect on the measured outcomes. By contrast, increasing final shear hurt filler retention and made the resulting paper more uniform. However, the final shear level did not have a significant effect on the tensile strength of the resulting handsheets. Medium-charge density cationic starch, used in pretreating the NFC, consistently gave greater strength in comparison to a high-charge cationic starch. The significance of these findings is that though the relatively high hydrodynamic shear levels associated with modern paper machines can have some beneficial effects, they do not necessarily overcome all challenges associated with wet-end addition of nanocellulose in combination with other additives.

Application: Modern papermaking systems, including pressure screens, additive injection systems, and headbox systems, can affect the levels of hydrodynamic shear to which the furnish is exposed after the addition of different chemical agents. A laboratory device called the Wet End Process Simulator (WEPS) can help predict the effects of different shear levels on retention, dewatering, and paper properties.

Papermakers have some limited, but low-cost, options regarding the intensity and time of hydrodynamic shear to which papermaking fiber suspensions are exposed after the successive injection of different dissolved or dispersed chemical agents. For example, they can inject an acrylamide-type copolymer retention aid solution either before or after a pressure screen [1]. They also can make use of modern devices that allow excellent mixing of additives very soon before the headbox of the paper machine [2,3]. Alternatively, a retention aid solution can be injected using a ring header or simple flange fitting connected to the approach flow piping of a paper machine. Such options make it meaningful to consider how changes in hydrodynamic shear might be incorporated into a papermaking strategy. By such means, one might aim to achieve an optimum balance between the rate of dewatering (which sometimes limits the production rate on a paper machine) and various aspects of paper quality.

As has been shown by Britt and Unbehend [4,5], the intensity of agitation of papermaking furnish before and during the formation of a paper sheet can have large effects on fine particle retention. Such effects have been attributed to the progressive breakdown of polymer bridges holding fine particles onto the fiber surfaces in the fiber suspension [5,6,7]. Such bridges result from the injection of chemical additives to the furnish, including very high molecular mass copolymers of acrylamide. Cationic starch also has been shown to play a role in the retention of fine particles [8]. However, what is beneficial for retention of fine particles sometimes has adverse effects on other outcomes of papermaking practices. Thus, it has been shown that some conditions of retention aid chemical usage can negatively affect the rate of water removal by vacuum [9]. In principle, a heavily flocculated furnish, in which many of the fibers are clustered together, provides easy paths for water to flow between the flocs, giving rise to rapid initial dewatering, as shown in the cited work. At later stages of vacuum dewatering, air likewise passes around the fiber flocs, with the wastage of vacuum pumping energy. Water remaining within the flocs appears to explain why poor vacuum dewatering may be observed in such cases. As shown by Roberts et al. [10] even treatment of pulp furnish with cationic starch can create sufficient flocculation such that very weak paper results at low levels of agitation. In fact, follow-up work by Britt and Unbehend [9] showed that more effective water removal by vacuum was achieved by application of hydrodynamic shear, after the addition of a flocculant and before the headbox, in preparation for the forming the paper.

Questions regarding effects of hydrodynamic shear had arisen in the course of earlier research carried out at North Carolina State University regarding the preparation of paper handsheets from recycled copy paper with the addition of cationic starch, nanofibrillated cellulose (NFC), cationic acrylamide copolymer retention aid, and some other optional additives [11-13]. In some of that work, it had been suggested that certain observed effects might have been different in a full-scale papermaking operation [12,13]. It had also been suggested that the hydrodynamic shear would likely have been higher than the levels that were employed in the cited laboratory studies. However, the laboratory work described in the cited articles did not explicitly compare different levels of agitation.

At TAPPI's 2023 PaperCon conference, the Sam Bo Scientific Co. Ltd. (Seoul, Republic of Korea) demonstrated its Wet End Process Simulator (WEPS) device. The WEPS can vary applied agitation over a very wide and reproducible range, while enabling formation of handsheets with highly reproducible uniformity and freedom from fiber orientation problems. Earlier publications based on the WEPS device appeared in 2002 and 2017 [14,15]. The WEPS incorporates several innovative design features. The furnish is agitated by six impellors, three rotating in one direction and three in the other. At the moment of release of the furnish onto the forming fabric, there is a pool of water resting on the surface of the forming fabric; this feature provides for about one second in which the fibers can stop swirling and adopt random orientations. Then, during vacuum dewatering, the device is subjected to a vertically oriented "shake," which is analogous to procedures used for many centuries by skilled hand papermakers [16,17]. In addition to the handsheets, the WEPS device provides information about rates of vacuum-induced drainage, as well as the final permeability of the wet handsheet at the end of the drainage process.

The present work involved not only the WEPS device, but also some parallel tests to quantify the retention of fines, the intensity of fiber flocculation in the slurry, the uniformity of formation in the resulting handsheets, and various other properties of the paper. Independent variables, in addition to hydrodynamic shear, included the levels of cationic starch (with two different charge densities of starch considered); the type of NFC (ordinary freeze-dried NFC or TEMPO-oxidized NFC, with a default addition of 5 parts per 100 parts of furnish solids); and the optional usage of cationic acrylamide copolymer (cPAM) retention aid.

Based on previous work (though different from the present work in many details), the authors considered the following hypotheses: It is proposed that increasing levels of hydrodynamic shear, before formation of the paper sheet, will make the resulting paper more uniform and less flocculated. It is further proposed that the more uniform paper will have a higher resistance to passage or water or air through it at different stages in the process. In other words, a decreasing freeness with increasing levels of hydrodynamic shear in the course of paper preparation was anticipated, and the resulting sheets were expected to be less porous. Finally, it is proposed that the strength of the paper would increase with increasing hydrodynamic shear levels as a result of increased uniformity. This is the first time a study has been devoted to the effects of hydrodynamic shear on papermaking outcomes involving addition of nanocellulose pretreated by cationic starch that uses equipment able to form paper and to measure dewatering rates over a very wide range of shear.

EXPERIMENTAL

Fiber sources and pulp preparation

The fiber source was Boise Aspen recycled multi-use paper (Boise Paper; Boise, ID, USA), which has 100% recovered fiber content. Past work has shown that the paper (all from the same carton) contains 22.7% of calcium carbonate ($CaCO_3$) filler by dry mass [18]. The pulp was dispersed in tap water using a laboratory Hollander beater (Voith; Heidenheim, Germany) with no load applied, such that the mixture having a consistency of about 2% was "brushed" for 30 min. The pulp was then diluted to slightly more than 0.5% solids. The electrical conductivity was raised to 1 mS/cm by addition of sodium sulfate (Na_2SO_4) solution at about 5% solids content.

Chemical preparation

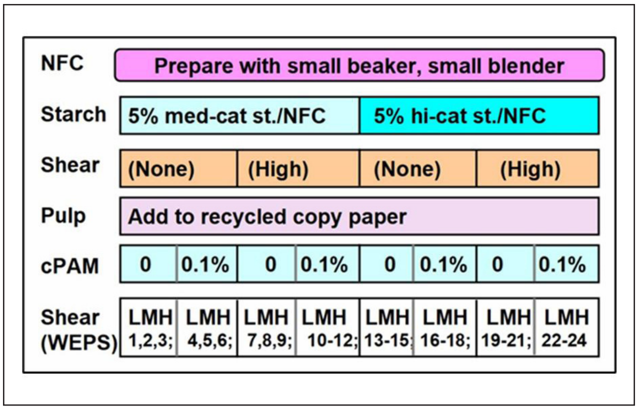
Chemicals employed in this work included two cationic starch products: 1) a non-commercial corn starch sample from an anonymous source with a medium charge density and a nominal degree of substitution of about 0.03; and 2) Grain Processing Corp.'s (Muscatine, IA) Chargemaster L340, a starch sample with high charge density and a degree of substitution around 0.20. The two starches were prepared for use by dissolution in hot water to a solids content of 1%. After stirring for 1 h, the starch solutions were allowed to cool to room temperature before use.

Two types of nanofibrillated cellulose (NFC) were obtained from the University of Maine, namely freeze-dried (default) and TEMPO-oxidized, both in dry form. Suspensions were prepared at a solids content of 0.5% and an electrical conductivity of 1 mS/cm, which was achieved by adding Na_2SO_4 as an approximately 5% aqueous solution.

The cationic acrylamide copolymer retention aid (cPAM) in dry-bead form was a product of American Cyanamid Corp. (Wayne, NJ, USA). It was prepared at the 0.1% solids level in deionized water with 1 h of brisk stirring.

Typical chemical addition sequence

Figure 1 describes the sequence of a typical experiment from the standpoint of chemical treatments. Conditions such as types of additives, dosages, and orders of addition



1. Typical example of a sequence of chemical addition and levels of hydrodynamic shear used in the present work (NFC: nanofibrillated cellulose; cPAM: cationic polyacrylamide; WEPS: Wet End Process Simulator; LMH: low/medium/high).

were in many cases the same for sets of experiments carried out with the three devices used to prepare and analyze samples, which are described in the following sections. These include devices to analyze dewatering rates and prepare handsheets; evaluate fine particle retention; and degree of fiber flocculation in the suspension.

In Fig. 1, the order of addition is represented by the direction of top to bottom, whereas the horizontal direction indicates different optional conditions for each indicated variable. Thus, in a typical experiment, the NFC was first treated at the 5% (by solids) level with a selected cationic starch product. In the series of tests represented in Fig. 1, the cationic starch-NFC mixture was either not exposed to high hydrodynamic stirring (only being mixed gently) or placed in a 250 mL Waring blender unit (Waring Products; Stamford, CT, USA) and exposed to 30 s of blending at the high level. Next, the treated NFC was added to the default fiber furnish such that the amount of NFC represented 5 parts per 100 parts of furnish solids. Each of the resulting mixtures was then optionally treated with cPAM at the 0.1% level based on solids. Finally, in the course of the test procedure, the pulp suspension was subjected to either low, medium, or high shear, as specified later in graphs or tables. While Fig. 1 gives an overall idea of the sequences employed, it does not include all of the options considered, such as some tests in which cationic starch was omitted.

Wet-end process simulator (WEPS)

Evaluation of vacuum-induced dewatering rates, resistance to air permeation after dewatering, and a range of tests of the resulting paper handsheets were carried out using the Wet End Process Simulator (WEPS) device supplied by Sam Bo Scientific Co. Testing followed the instructions provided in the manual for the device. An 80-mesh plastic screen was employed as the forming fabric. The chemical addition sequences were arranged with selected "low" (400 rpm), "medium" (1000 rpm), and "high" (1700 rpm) agitation levels. Each addition of a chemical was followed by 10 s of agitation at a planned level. The WEPS device was programmed to record the slope representing the rate of drainage, as well as a final vacuum level indicating resistance to air flow through the damp paper sheet at the end of the dewatering cycle.

Once sheet formation was completed, the sheets were peeled from the forming screen, placed between sheets of blotter paper, covered with a smooth rigid stainless-steel sheet, and rolled against a hard, flat laboratory bench with the type of roller described in TAPPI Standard Test Method T 205 "Forming handsheets for physical tests of pulp." The handsheets were next pressed against polished chrome discs with the use of blotter paper, again following TAPPI T 205. The same standard was used for drying the sheets under tension using the stacked rings, noting that the sheets were somewhat larger (diameter 19.5 cm) than those described in the TAPPI T 205 method.

Retention tests

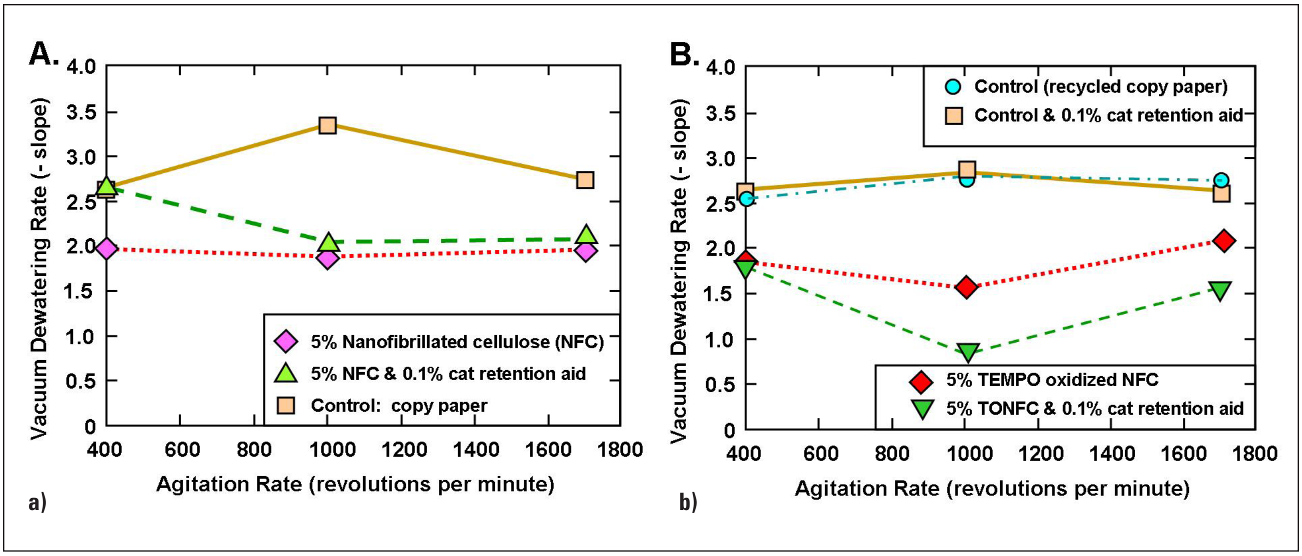
The efficiency of fine-particle retention during paper formation was evaluated using a Britt jar [4,5]. A 200-mesh screen was employed. For a typical set of experiments, the agitation was adjusted in different tests to "low," "medium," and "high" levels, which will be specified later when results are presented. The high level was achieved by using a kitchen blender, after which the furnish was poured into the Britt jar. Further details about the procedure for evaluating retention efficiency have been described by Garland et al. [11].

Flocculation tests

The level of flocculation in fiber suspensions, both before and after treatment with different chemical types, dosages, and orders of treatment, as well as with consideration of hydrodynamic shear levels, was determined using a photometric dispersion analyzer (PDA), which was the low-gain version distributed by Rank Brothers (Newbury, UK). Root-mean-squared values related to the fluctuation of transmitted light passing through a 6-mm internal diameter Tygon tube were evaluated using both gain constants set to 1.000 and with the filter option active.

Tensile testing

Tests of the tensile properties of the formed handsheets were done in accordance with TAPPI T 494 "Tensile properties of paper and paperboard (using constant rate of elongation apparatus)" and TAPPI T 220 "Physical testing of pulp handsheets." The paper was equilibrated for at least 24 h at 23°C and 50% relative humidity. A horizontal tensile tester, Model 84-56-00-003 from Testing Machines Inc. (New Castle, DE, USA), was used to break sets of 15-mm-wide strips of paper cut from the centers of the handsheets. The clamps of the device had an initial span of 100 mm. The device reported the breaking length (theoretically, the length sufficient to cause self-breakage by gravity), the per-



2. Vacuum dewatering rates determined as the negative values of the slopes reported by the WEPS device for 0.5% suspensions of default furnish optionally containing either (a) conventional freeze dried NFC or (b) TEMPO-oxidized NFC at the 5% level on furnish solids, or with further optional treatment with cationic retention aid.

cent stretch to breakage, and some other related quantities.

Air permeability of the dry paper

TAPPI T 460 “Air resistance of paper (Gurley method)” was used to assess the permeability of the handsheets to air. Results of such tests can be important when attempting to develop or manufacture paper products to meet barrier performance targets. Even if the final barrier properties depend on one or more coating layers, the pore structure of the base paper can be expected to play an important role. In the present work, the Gurley densometer test results also served as a way to corroborate observed effects on the final vacuum level of the damp paper, as described earlier.

Formation uniformity of the paper

The uniformity of the paper in a size range of 6.7–13 mm (range C7) was assessed with a Paper PerFect Formation Analyzer from OpTest Equipment Inc. (Hawkesbury, ON, Canada). This setting was selected because it is distinctly longer than the longest individual wood pulp fiber, making it possible to attribute such features to flocs of fibers.

Filler content

The ash content of the handsheets was tested and used to compute the filler content. As described in TAPPI T 413 “Ash in wood, pulp, paper and paperboard: combustion at 900°C,” the handsheets were weighed and put in tared crucibles in an oven that was then heated to 900°C and held for at least 1 h and then removed and weighed again after cooling. Results were calculated based on an assumption that $CaCO_3$ was the only mineral present in the air-dried paper (which had a moisture content of approximately 5% to 6% at 50% relative humidity). The ignition factor was calculated based on the molecular masses of calcium oxide (CaO) at 56.08 g/mole and $CaCO_3$ at 100.08 g/mole, which implies the following relationship:

Filler (%) = 100 * (100.08/56.08) * (Ash mass/Paper mass)

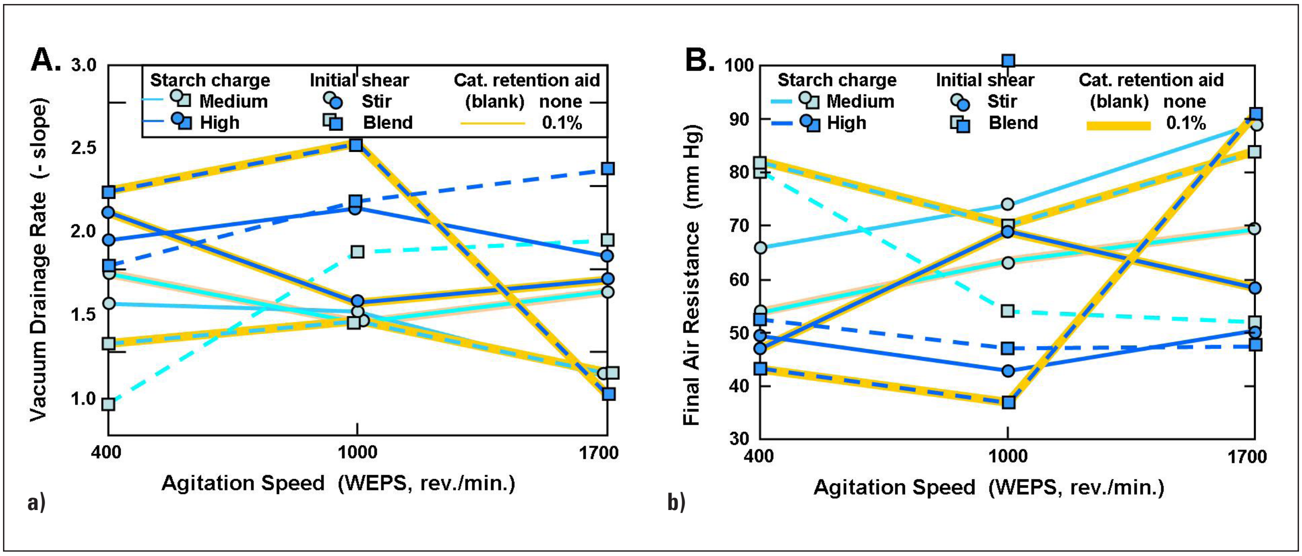
RESULTS

Dewatering rate

Vacuum-induced dewatering rates were calculated by the WEPS device using the slope of the dewatering line measured during the handsheet making process. In **Fig. 2**, the dewatering rates of control samples, samples with only NFC or cPAM, and samples with NFC and cPAM are compared at three different levels of shear. The NFC was added at a 5% level, and the cPAM was added at a 0.1% level based on solids for both experiments represented.

Figure 2a shows the dewatering rates when freeze-dried NFC (FDNFC) was used. Each point represents the average dewatering rate of three replicates. As expected, the control had the fastest drainage results. It can be observed that the addition of FDNFC slowed the drainage significantly, but further addition of the cPAM along with the FDNFC did not have much effect, except at the low shear level. The drainage was likely recovered in that case due to the tendency of cPAM to overflocculate the system at low agitation.

Figure 2b shows the dewatering rate results when TEMPO-oxidized NFC (TONFC) was used. Each point represents the average dewatering rate of four replicates. Once again, the control resulted in the highest dewatering rate, and the addition of only cPAM had little effect. When only TONFC was added to the system, it again resulted in a much slower dewatering rate. Adding TONFC had a slightly greater effect than FDNFC, which was most noticeable at the medium shear level. This difference could be attributed to the narrower fibrils in TONFC.



3. Vacuum dewatering rates for systems in which NFC had been pretreated with cationic starch at the 5% level on NFC solids, followed by optional blender shearing, before being added to the default furnish, with other conditions being the same as the previous figure.

The largest change in the dewatering rate occurred when both TONFC and cPAM were added to the system. The presence of both components strongly suppressed the drainage at a medium level of shear. At a higher level of shear, some of the drainage loss was recovered. This could be due to an interaction between cPAM and TONFC in which the TONFC particles are made into bigger clusters and are more effective in choking drainage channels. It could also be explained if the NFC in the system was retained in the sheet rather than just passing through. This would be consistent with the fact that filler particles do not seem to have much effect on dewatering because they are too small to be effective in blocking drainage channels. It was found that a high shear level was able to break down whatever was responsible for slowing down the drainage.

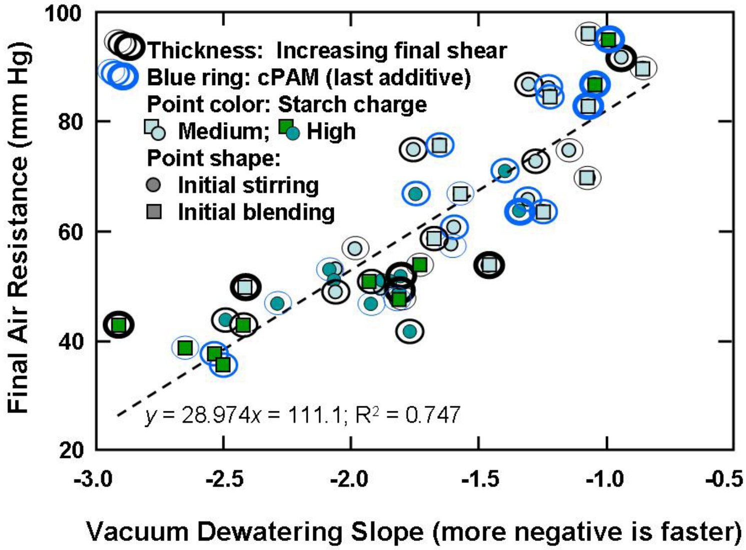
Figure 3 shows another experiment performed using the WEPS device, where the type of cationic starch, level of initial shear, cPAM addition, and level of final shear were varied among samples with TONFC present. Medium- or high-charge cationic starch was added at a 5% level based on solids, and the samples were either blended or stirred before being added to the WEPS device. The same agitation rates were used, and cPAM was added at a 0.1% level based on solids if included. Two replicates of each condition were tested.

Figure 3a shows the vacuum dewatering rate found for each condition. When comparing specific conditions, the effects of the level of flocculation on drainage can be observed. Certain conditions, such as the inclusion of high-charge cationic starch, blending during preparation, and cPAM, can lead to a high level of flocculation in the system. Under these conditions, application of medium shear improved the dewatering rate to be the highest of all the conditions tested. Conversely, application of high shear led to a much lower dewatering rate and very poor drainage. This suggests that there may be an optimum degree of flocculation in a system relative to dewatering performance.

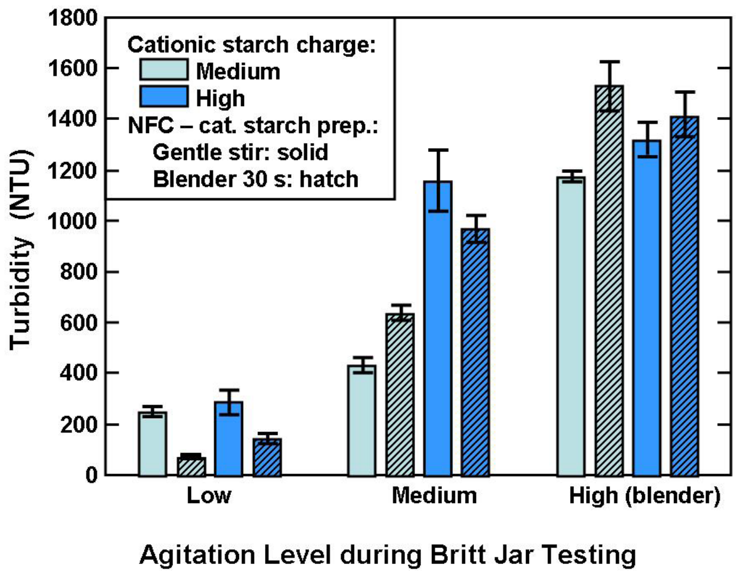
In most cases, a medium level of shear improved the dewatering rates compared to a low level of shear, which was consistent with the results of Britt and Unbehend [9]. However, a couple of curves in Fig. 3 showed the opposite trend. In both conditions, the samples had been stirred instead of blending during preparation. For one condition, medium-charge starch was used, and for the other, high-charge starch was used. For both curves, the dewatering rate was shown to decrease with the application of medium shear, but increase and recover some of the drainage with the application of high shear.

Figure 3b shows the final air resistances in millimeters of mercury (mm Hg) measured by the WEPS device after vacuum dewatering. The final air resistance results showed a high correlation with the vacuum drainage rate results. An coefficient of determination (R^2) value of 0.747 shows that approximately three-quarters of the variance in the data can be explained by the close relationship between the two variables.

The strong correlation between the vacuum dewatering rate and final air resistance that was apparent from Fig. 3 can be more clearly observed in **Fig. 4**. The highest drainage was found when the final air resistance was the lowest. This is consistent with the principle that the highest rates of dewatering tend to be correlated with a lower final air resistance. One might expect that a faster drainage rate would be associated with bigger channels through the paper for both water and air, and a lower air resistance could be measured. Indeed, correlations between drainage rates and permeability have been reported in a few cases [19,20].



4. Correlation between final air resistance (vertical axis) and vacuum dewatering slope (horizontal axis).

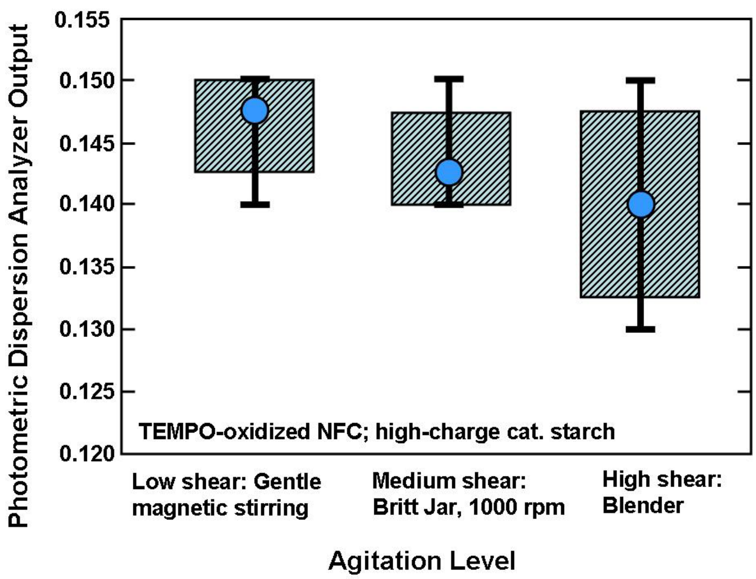


5. Filtrate turbidity from Britt jar tests, depending on the charge density of cationic starch (see depth of blue color), and the severity of agitation following NFC treatment with the cationic starch (with hatch pattern indicating blender treatment).

The cause of this dependency can be further investigated by observing the trends present in Fig. 4. Increasing the final shear on the WEPS did not have a consistent trend, and initial stirring vs. blending did not have a significant effect. It was found that high shear after cPAM addition gave slow dewatering and high final air resistance, and that some of the high-charge cationic starch conditions resulted in the highest drainage and lowest final air resistance. Overall, it was shown that high-charge starch was more effective than the medium-charge starch in promoting drainage and air permeability of the wet web.

Retention

Britt jar testing was performed to evaluate the fine-particle retention under different conditions. **Figure 5** shows the results of an experiment in which the agitation level during Britt jar testing and the charge of cationic starch added were varied. For all cases, FDNFC was present and treated with either medium- or high-charge cationic starch at a 5% level based on solids. The FDNFC was then added to the stock. For half of the conditions, the FDNFC and starch mixture was blended before addition. The other half received no initial blending before addition to the stock. The agitation levels during the testing included low, medium,



6. Level of fiber flocculation, as represented by photometric dispersion analyzer (PDA) output for default furnish with 5% of TEMPO-oxidized NFC that had been pretreated with high-charge cationic starch, followed by three levels of agitation.

and high. Turbidity readings were collected ten times at each condition.

As shown in Fig. 5, increasing the shear in the Britt jar clearly increased the turbidity of the filtrate tested for all conditions. This was true regardless of cationic starch charge used or application of pre-shearing. It can be observed that high-charge cationic starch was more shear-sensitive and the turbidity readings increased more drastically at the intermediate level than for the medium-charge starch. This suggests that the high-charge cationic starch was functioning as a weak bridging agent, and the effects were more readily disrupted by increasing shear. It is worth noting that $CaCO_3$ filler has a much more major light scattering ability than NFC or fiber fines, on a weight basis. For these tests, there was more $CaCO_3$ present in the suspension than NFC or fiber fines.

Flocculation and formation uniformity

Figure 6 shows the results of an experiment in which the level of flocculation was measured for a control stock with no additives. Low, medium, and high levels of shear were used. These levels were achieved through gentle stirring with a magnetic bar, Britt Jar stirring at 1000 rpm, and a blender, respectively.

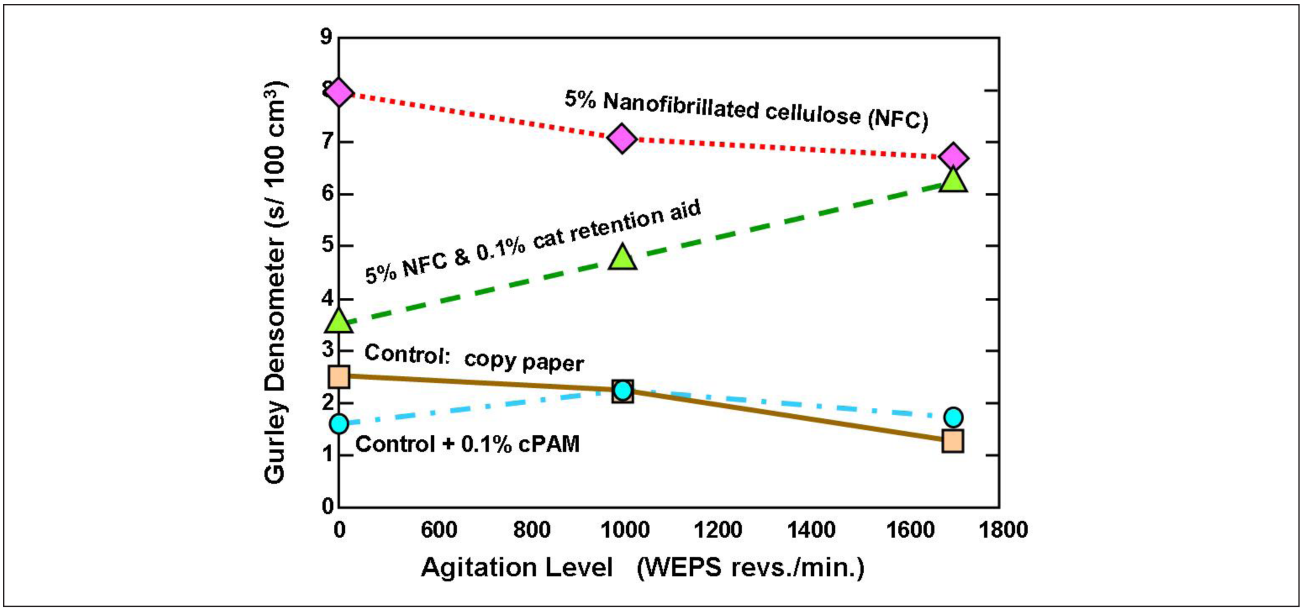
All the reported values were within the low-to-moderate range for flocculation. From the results, there was no cause for concern about over-flocculation. There was a slight downwards trend for the PDA output as the shear level increased, and the lowest PDA outputs were found at the highest level of shear. This would be consistent with the effect of shear breaking up flocs in the suspension, but the effect of shear was not statistically significant for this measurement.

Sheet porosity

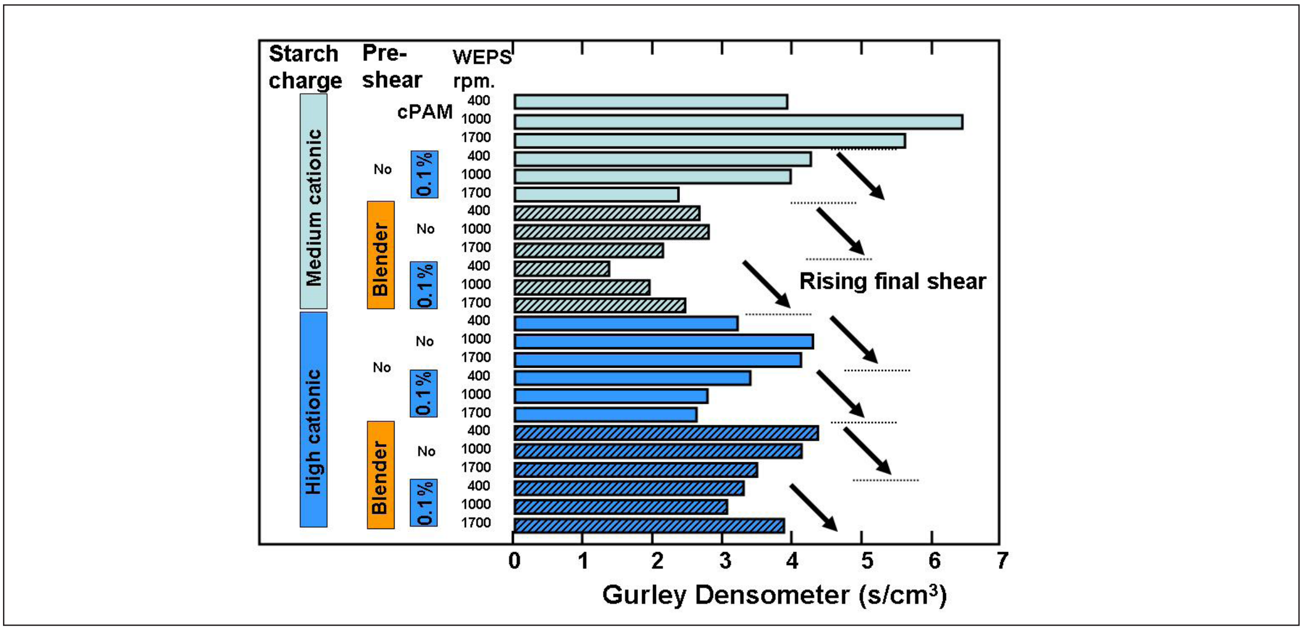
Figure 7 shows the Gurley densometer results for handsheets made in the same experiment represented in Fig. 2b. This includes control samples, samples with only FDNFC or cPAM, and samples with FDNFC and cPAM; these are compared at three different levels of shear. The FDNFC was added at a 5% level, and the cPAM was added at a 0.1% level based on solids for both experiments represented. The agitation rates used during the process were 400 rpm (low shear), 1000 rpm (medium shear), and 1700 rpm (high shear).

The porosity of the control group was not significantly affected by the level of applied hydrodynamic shear. However, the addition of FDNFC to the sheets greatly increased the Gurley seconds, therefore reducing the sheet porosity. This was true at all levels of shear for conditions with FDNFC added alone and for conditions with FDNFC and cPAM added together at higher levels of shear. The results for FDNFC added alone are consistent with the Kozeny-Carman explanation, where the idea is that NFC filled voids in the sheets with strands laying across passages and created friction against the air as it passed [21,22]. The effect of the cPAM is consistent with a bridging mechanism that makes the NFC lie down on fiber surfaces and prevents it from blocking the passages in the sheet [23]. With increasing shear, the effect of that mechanism was lost. These results are consistent with the breaking of bridges at higher agitation levels.

The porosity of sheets for a wider range of conditions was also tested. For the data represented in **Figs. 8–11**, the charge of cationic starch added, application of pre-shearing, cPAM addition, and WEPS agitation level were varied when creating the handsheets tested. Two replicates of each condition were evaluated.



7. Gurley densometer (resistance to air permeation) values for handsheets prepared under conditions corresponding to Fig. 2a, where the horizontal axis gives the agitation in the WEPS device.

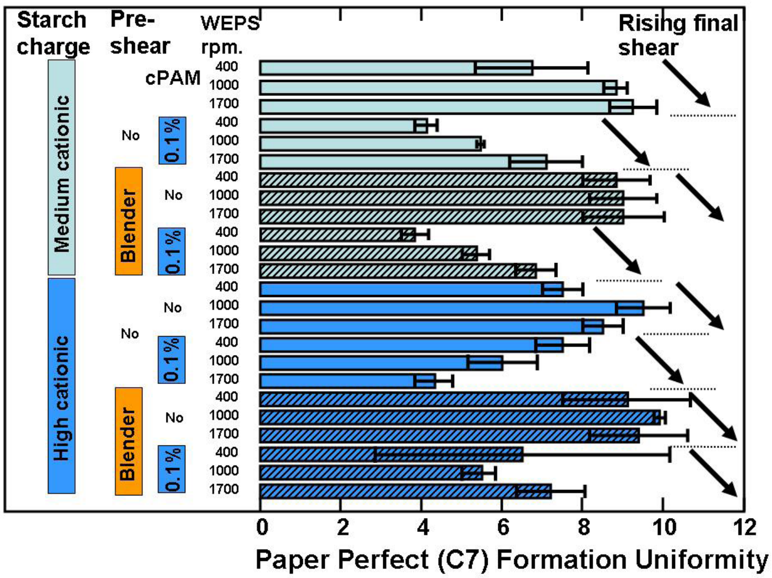


8. Gurley densometer results corresponding to tests in which the NFC had been pretreated with cationic starch (two charge densities) at the 5% level based on solids, followed by optional cPAM treatment (zero or 0.5% levels), and finally, different levels of agitation before sheet formation.

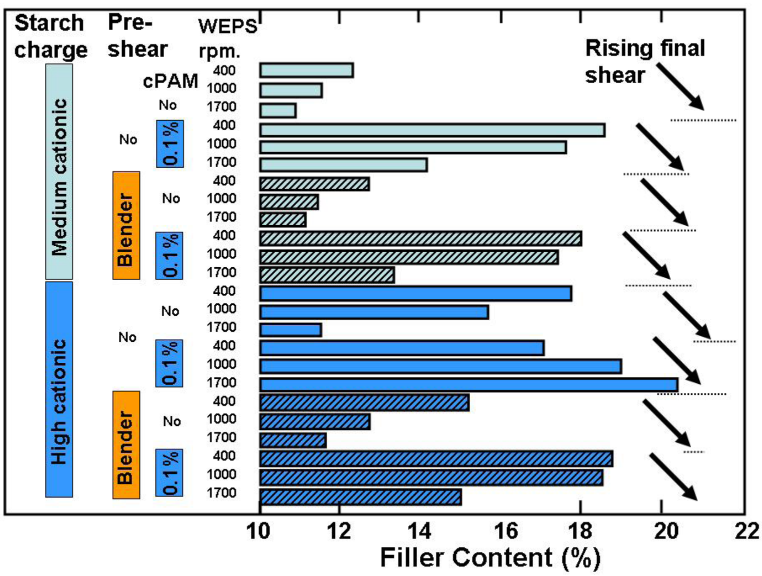
A few important trends can be observed in Fig. 8. For example, for conditions with medium-charge cationic starch and no cPAM, the highest Gurley densometer seconds measured were at a medium level of shear. Furthermore, higher Gurley densometer seconds were measured when the initial mixture of medium-charge cationic starch was stirred rather than blended. It can also be seen that the addition of cPAM tended to decrease the Gurley densometer measurement moderately. It could be inferred that this is because a less uniform sheet resulting from flocs created by the cPAM would be less effective in blocking air with all other conditions equal.

Handsheet uniformity

It can be observed in Fig. 9 that for tests involving medium-charge cationic starch, increasing shear consistently improved formation uniformity. The effects of shear for tests involving high-charge cationic starch were mixed. The combination of high-charge cationic starch, with no preshearing but with cPAM addition, had particularly poor



9. Formation uniformity of handsheets as a function of sheet-forming conditions corresponding to Fig. 3 and Fig. 8.



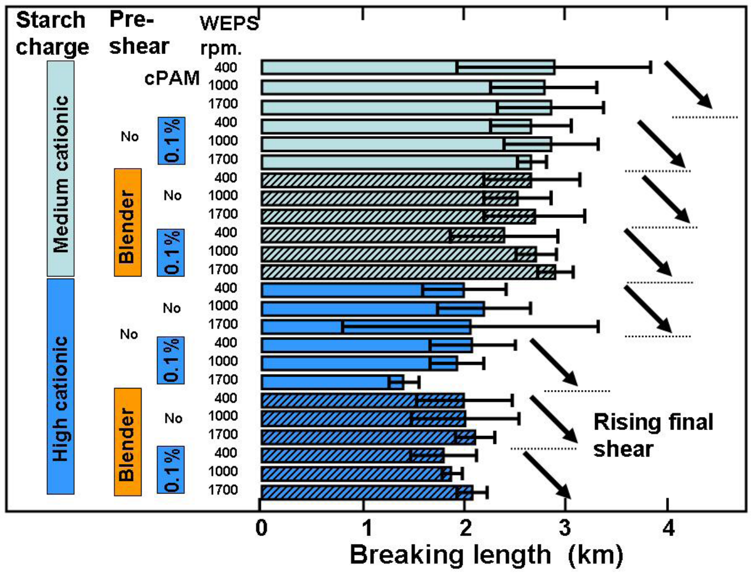
10. Filler content, as determined by ashing the air-dried (approximately 6% moisture content) handsheets at 900°C, assuming that $CaCO_3$ was the only mineral present, and that CaO was the only mineral after washing.

uniformity at high shear. This was likely due to an excess of cationic flocculation if the high-charge cationic starch can be counted as contributing to the action of the cPAM, especially in the absence of pre-shearing. For both the medium and high-charge starch, adding cPAM consistently hurt formation uniformity.

Paper moisture and filler content

As shown in Fig. 10, among almost every successive group of three, with increasing WEPS shear in each set, a consistent trend in filler content of the paper can be observed in which the filler content decreased with increasing shear level. This trend is consistent with Britt jar findings. Notably, there was one group of three that instead showed the opposite trend. For handsheets made with high-charge cationic starch, no pre-shearing, and cPAM added, the filler content increased with increasing shear. In this case, it may be possible that there was so much "cationic flocculant" present (if the high-charge cationic starch is considered as a flocculant) that the high shear condition was more optimum.

When the moisture at every condition was investigated, it was found that there was a correlation between the paper



11. Tensile breaking length of handsheets, based on the same set of variables. Tensile breaking length of handsheets, based on the same set of variables.

moisture and filler content. The lower the filler content, the higher the moisture content of the paper. This was likely due to the fact that filler does not absorb significant moisture. However, there were clearly other factors involved based on the amount of variation in results. It is possible that the amount of hydrophilic NFC in the sheet could be correlated with some of the other factors promoting retention of the filler in different ways.

Paper strength properties

Figure 11 shows the breaking length data collected for the varying conditions. The most significant difference can be seen when comparing the results when using medium-charge vs. high-charge cationic starch. The medium-charge starch was much more beneficial for strength overall.

The effects of other variables were not as notable. Both increasing WEPS shear level and pre-shearing the NFC and starch mixture had no significant effect on the breaking length. The handsheets made with high-charge cationic starch, no pre-shearing, cPAM added, and a high shear level were observed to be outliers when considering these trends.

Furthermore, the use of cPAM did not appear to have any significant consequences on strength. If adding cPAM had resulted in more filler or higher flocculation, then the effect must have been compensated by higher retention of bonding agents such as NFC and cationic starch in the paper, rather than just filler. If filler alone had been retained, the strength of the sheet would have been hurt.

When correlating the breaking length of the paper to filler content, it could still be shown that the biggest influence on the data was the charge density of the starch. The regression of the data showed an R^2 value of 0.2582, but it seemed that most of the effect could be attributed to the strength differences caused by the charge of the starch. It was found that the conditions that maintained good strength at a higher range of filler content were with medium-charge cationic starch, use of cPAM, and a medium WEPS shear level. There was also a moderate preference for not pre-shearing the cationic starch and NFC before addition to the stock.

It was also found that there was a very weak dependency of breaking length on formation uniformity. Only the very worst formation in each set of conditions with the same starch used gave a lower breaking length than the rest. The high-charge cationic starch data points were all below the regression line created, indicating lower strength, and the medium-charge cationic starch data points were all above the regression line, indicating higher strength. This is consistent with the other data collected.

DISCUSSION

Setting a challenge

From the papermaker's standpoint, the present work considered a set of challenging circumstances. A 5% level of very highly fibrillated cellulosic material (the NFC) can be expected to greatly suppress dewatering on a paper machine [24,25]. The approximately 22% of mineral content present in the default furnish (repulped 100% recycled fiber content copy paper) placed a severe test on the ability of different combinations of additives to act as retention aid systems. The pretreatment of the NFC with either of two types of cationic starch, followed by optional application of intense hydrodynamic shear, provides a novel aspect to this work. In general, the dosages of additives, including the dosage of cationic retention aid (0.1% cPAM on furnish solids, dry basis) were intentionally selected to be on the high side in this work, with the goal of yielding statistically significant differences in various outcomes. Thus, a disclaimer is in order: One should not regard the recipes presented in this work as templates for industrial production. Rather, the goal here has been to consider the extent to which some well-established principles regarding papermaking technology continue to hold true during paper formation when introducing such innovative features as cationic starch-pretreated NFC; strongly different charge densities of cationic starch; and widely different levels of hydrodynamic shear.

Textbook examples

A textbook example can be defined as a set of circumstances that conform to some well-established theory. Based on that definition, the present work has provided several textbook examples as follows:

As shown in Fig. 9, increasing hydrodynamic shear tended to make the resulting paper more uniform, in most cases. This is consistent with the breakage of polymer bridges, such as those expected when papermaking furnish is treated with cPAM [6,7,26], as well as general dispersion of suspended matter by shearing [27,28].

As was shown in Fig. 5, increasing hydrodynamic shear also decreased fine particle retention, as indicated by increasing turbidity of filtrate in Britt jar tests. This trend was confirmed by a decreasing content of mineral in the resulting paper (Fig. 10). Again, the findings can be explained by the breakage of polymer bridges and general dispersion of particles by shear [27,28].

As shown in Fig. 2, the presence of NFC dramatically slowed the rates of dewatering. As noted earlier, this is consistent with theories of the blockage of drainage channels [23]. It is also consistent with the Kozeny Carman theory [21,22], which predicts slower drainage in cases where a filter medium (i.e., the paper) has a higher specific surface area.

As shown in Fig. 4, there was a very strong correlation between water permeability (i.e., the vacuum drainage rate) and air permeability (as represented by the final vacuum level in the WEPS test cycles). Though this makes logical sense, such a relationship has seldom been reported in scholarly studies.

Unexpected findings

Learning can take place when there are unexpected experimental results, or especially when results fail to conform to widely-held rules of thumb. One such unexpected finding was a strong dependency of paper strength on the charge density of cationic starch that had been used to pretreat the NFC. Earlier tests had shown highly promising results when a high-charge cationic starch had been used to pretreat NFC before addition to a bleached kraft pulp suspension prepared with low levels or lack of mechanical refining [29]. However, as was shown in Fig. 11, pretreatment of the NFC with medium-charge cationic starch (having a degree of substitution of 0.03) invariably provided higher handsheet tensile strength in comparison to similar treatment with the high-charge cationic starch (degree of substitution 0.2). As a possible way to explain this difference, it is tentatively proposed that the high-charge starch is expressing behavior similar to that of a cationic retention aid, which it more closely resembles in terms of its charge density. Such behavior would include a greater flocculation tendency in comparison to the other cationic starch, which is more typical of what papermakers employ as a bonding agent. A more flocced structure within paper would be expected to make it weaker [30]. However, such an explanation does not explain all of the results of the present study. For instance, as noted earlier, there was almost no correlation between the breaking length of handsheets prepared in this work and the formation uniformity of the paper.

A second way to possibly account for the same observations became apparent in work published by Rao et al. [31]. The cited authors studied effects of adding either cationic or conventional anionic precipitated calcium carbonate (PCC) particles to NFC suspensions, followed by dewatering, to form a film. As in the present work, it was found that the cationic PCC promoted dewatering. Also, in parallel to the present work, the addition of cationic PCC yielded lower strength when compared to similar NFC films prepared with the same amounts of anionic PCC. The cited authors suggested that the electrostatic interactions between the cationic PCC and the anionic NFC may have been effectively replacing potential hydrogen bond formation within the films, which would be a way to account for the lower strength.

Another unexpected finding was that it did not appear to matter whether or not blending action (i.e., pre-shearing) was applied immediately after pretreating NFC with cationic starch. As was shown in Fig. 1, one of the goals of the study was to demonstrate such effects. The plan was to at least allow the possibility for redispersion of clumps of NFC and cationic starch if their initial mixing had caused flocculation or entanglement. In theory, an excess of cationic starch could alternatively act as a stabilizer for the NFC, allowing it to remain in an extended form, rather than being clumped up. Different hypotheses to explain why pre-shearing did not seem to matter can be listed as follows: a) initial mixing of the cationic starch and NFC actually did not change the form or degree of clustering of the NFC; b) initial mixing of the cationic starch and NFC bound them together in such tight flocs that they remained clustered regardless of later application of intense hydrodynamic shear; or c) any effects that might have been produced by pre-shearing were overwhelmed by subsequent processing steps, which sometimes included high levels of hydrodynamic shear applied to the complete furnish in the presence of all of the additives.

As shown in Fig. 11, a third unexpected finding was the fact that increased final application of hydrodynamic shear just before forming the sheet did not appear to affect the strength of the paper. This is despite the fact that increased shearing both made the paper more uniform (Fig. 9) and decreased the filler content (Fig. 10). Past work has shown a strong relationship between paper strength and uniformity in systems where the main independent variable was retention aid type and dosage [30]. In addition, it is well known that increasing mineral content of paper tends to hurt its strength [32,33]. In simple furnish systems, a filler particle would tend to interfere with some of the bonding between adjacent fibers in paper [34]. A possible hypothesis, attempting to explain the current findings, is that factors that tend to retain filler in the paper (including lower shear levels) could also encourage retention of more NFC, which would be presumed to act as a bonding agent. However, once again, the present article does not provide sufficient evidence to judge one way or the other on the suggested mechanism.

Needed future work

Unexplained findings in the present work, as just described, suggest a need to apply additional research tools. In particular, it would be helpful to have information about what is happening at a colloidal level [34]. The field of colloids is concerned with particles spanning the size range from mineral fillers to cellulosic fines. To this short list, it would be appropriate to add NFC, which is clearly in the colloidal size range. The tendencies of colloidal suspensions to coagulate or remain in stable suspension are known to be highly dependent on the ionically charged nature of the particles, as well as the charged nature of any polyelectrolytes or multivalent ions. All of these can be evaluated by either running titrations of the charge demand or measuring the zeta potential [34]. Tests also are needed to answer questions about the tendency of particles within a papermaking furnish to cling to each other on contact or to slide past each other, which is another aspect of colloidal stability. Finally, microscopic imaging is needed to answer questions already raised in this work about whether the cationic starch-pretreated NFC becomes clumped up, and if so, can such clumping be reversed by application of sufficiently intense hydrodynamic shear.

CONCLUSIONS

The foremost objective of this work was to test a hypothesis that changing the hydrodynamic shear at two points in a papermaking process would significantly affect paper strength and various other papermaking process outcomes. The selected furnish presented a set of challenging circumstances. The use of 100% copy paper provided a filler content of about 22% in the mixed furnish, thus making fine particle retention a challenging issue. By adding 5% of cationic starch-pretreated NFC to the furnish, dewatering became a serious issue. In addition, the whole series of tests was repeated for two different charge densities of the cationic starch used to pretreat the NFC.

With respect to the tensile strength of the paper, by far the most influential variable was the charge density of the cationic starch used to pretreat the NFC. All twelve of the experimental conditions involving the medium-cationic starch gave higher values of the tensile breaking length as compared to matched conditions with the high-charge cationic starch.

Variations in hydrodynamic shear gave mixed results. None of the output variables, including paper strength, was significantly affected by different levels of pre-shearing. By contrast, application of increased hydrodynamic shear to the complete furnish, just before forming the sheet, made the paper more uniform and decreased fine-particle retention. Despite these effects, which might have been expected to give stronger paper, there was no significant effect on the paper's tensile strength. Thus, more research is needed to be able to explain some of the results. **TJ**

ACKNOWLEDGEMENTS

The experimental work reported in this article represents the efforts of members of the Fall 2023 class of PSE 322, "Wet End & Polymer Chemistry" at North Carolina State University. These students, who included John A. Morrow, Gray B. Hardy, William D. Pearson, T.J. Ferry, Taylor P. Floyd, Erin M. Bracken, Benjamin T. Young, Tyler G. Gatewood, Conner N. Wrought, Caroline F. Youngblood, Brendan R. Marcy, David Rios Herrera, Brynn M. Price, Zack L. Carson, and Kaya J. Kusmeirczuk, are acknowledged for their contributions to the present work. The student coauthors Kensley V. Hamm, Lucy A. Jones, Varan S. Atree, and Daniel J. Kozel contributed to the work during the semester and also completed follow-up experiments, discussed the interpretation of the findings, and contributed to the writing. Dr. Jeong-Yong Ryu of Kongwon National University participated in discussions during and after the semester and helped with the writing. The work of Dr. Martin A. Hubbe is supported by the Buckman Foundation. The high-charge cationic starch was provided by Grain Processing Corp. The authors are grateful for the provider or the medium-charged cationic starch, who asked to remain anonymous.

LITERATURE CITED

1. Hubbe, M.A. and Wang, F., *TAPPI J.* 1(1): 28(2002).
2. Swales, D.K., "Mixology – Theory and practice as applied to papermaking," in *Advances in Papermaking Wet End Chemistry Application Technologies* (M.A. Hubbe and S. Rosencrance, Eds.), TAPPI Press, Atlanta, 2018, Ch. 3, pp. 43-67.
3. Käyhkö, J., Matula, J., Matula, J., et al., "Systems for feeding and mixing wet-end additives," in *Advances in Papermaking Wet End Chemistry Application Technologies* (M.A. Hubbe and S. Rosencrance, Eds.), TAPPI Press, Atlanta, 2018, Ch. 4, pp. 69-102.
4. Britt, K.W., *Tappi* 56(10): 46(1973).

5. Britt, K.W. and Unbehend, J.E., *Tappi* 59(2): 67(1976).
6. Hubbe, M.A., *Nord. Pulp Pap. Res. J.* 15(5): 545(2000). https://doi.org/10.3183/npprj-2000-15-05-p545-553.
7. Hubbe, M.A., *Nord. Pulp Pap. Res. J.* 16(4): 369(2001). https://doi.org/10.3183/npprj-2001-16-04-p369-375.
8. Glittenberg, D., *Tappi J.* 76(11): 125(1993).
9. Britt, K.W. and Unbehend, J.E., *Tappi* 63(4): 67(1980).
10. Roberts, J.C., Au, C.O., and Lough, C., *Tappi J.* 69(10): 88(1986).
11. 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.
12. 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.
13. 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.
14. Woo, Y.-K., Ryu, J.-Y., Kim, Y.-H.., et al., *J. Korea TAPPI* 34(4): 1(2002).
15. Lee, T.J., Lee, K.S., Lee, J.H., et al., *J. Korea TAPPI* 49(3): 102(2017). https://doi.org/10.7584/JKTAPPI.2017.06.49.3.102.
16. Hunter, D., *Papermaking. The History and Technique of an Ancient Craft*, Dover Publications, Mineola, NY, USA, 1947.
17. Hubbe, M.A. and Bowden, C., *BioResources* 4(4): 1736(2009). https://doi.org/10.15376/biores.4.4.1736-1792.
18. Putney, S., Seidel, I.H., Litavecz, M.S., et al., *TAPPI J.* 23(1): 67(2024). https://doi.org/10.32964/TJ23.2.67.
19. Lindström, T., in *Fundamentals of Papermaking, Trans. IXth Fund. Res. Symp., Cambridge* (C.F. Baker and V.W. Punton, Eds.), Mechanical Engineering Publications Ltd., London, 1989, p. 311.
20. McCourt, A.M., Ford, P.A., and Cauley, T.A., *Tappi J.* 776(10): 165(1993).
21. Kozeny, *Sitzungsber. Akad. Wiss. Wein, Math-Naturwiss. Kl.*, Abt. 2A, 136: 271(1927).
22. Carman, P.C., *Trans. Inst. Chem. Eng.* 16: 168(1938).

ABOUT THIS PAPER

Cite this article as:
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

DOI: https://doi.org/10.32964/TJ23.9.477

ISSN: 0734-1415

Publisher: TAPPI Press

About this journal

ABOUT THE AUTHORS

We studied this topic because great interest was shown by other participants at a PaperCon meeting regarding earlier articles in this series by our group. This research adds a new aspect – detailed evaluation of the effects of different levels of hydrodynamic shear.

The most difficult aspect of this study was that most laboratory tests are not run in such a way as to be able to evaluate levels of hydrodynamic shear. To address this issue, we used the Wet End Process Simulator (WEPS) device, which is newly available.

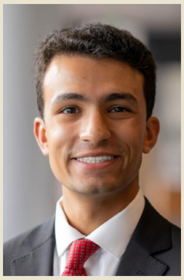
We found that nanocellullose does not necessarily follow expectations based on principles established for other wet-end additives. An interesting finding was that factors that would have been expected to increase paper strength did not show positive effects.

With the information in this study, papermakers can be on the lookout for challenges related to the dewatering of furnish to which nanofibrillated cellulose has been added. In order to more fully interpret the results from this study, colloid-chemical test results are needed. Those results are reported and discussed in a companion article.

Hamm

Kozel

Jones



Atree

Ryu

Hubbe

Hamm, Kozel, Jones, and Atree are affiliated with the undergraduate Paper Science and Engineering Program of the Department of Forest Biomaterials at North Carolina State University in Raleigh, NC, USA. Ryu is a professor in the Department of Paper Science and Engineering at Kangwon National University in Chuncheon-si, Gangwon, Republic of South Korea. Hubbe is a professor in the Department of Forest Biomaterials at North Carolina State University in Raleigh, NC, USA. Email Hubbe at hubbe@ncsu.edu.

23. Hubbe, M.A., Sjöstrand, B., Nilsson, L., et al., *BioResources* 15(4): 9672(2020). https://doi.org/10.15376/biores.15.4.Hubbe.

24. Balea, A., Fuente, E., Monte, M.C., et al., *Molecules* 25(3): 526(2020). https://doi.org/10.3390/molecules25030526.

25. Barrios, N., Marquez, R., McDonald, J.D., et al., *Adv. Colloid Interface Sci.* 318: 102936(2023). https://doi.org/10.1016/j.cis.2023.102936.

26. Lindström, T., Söremark, C., and Eklund, L., *Tech. Trans. CPPA* 3(4): TR114(1977).

27. Rojas, O.J. and Hubbe, M.A., *J. Dispersion Sci. Technol.* 25(6): 713(2004). https://doi.org/10.1081/DIS-200035485.

28. Hubbe, M.A., *BioResources* 2(2): 296(2007). https://doi.org/10.15376/biores.2.1.1-2.

29. Rice, M.C., Pal, L., Gonzalez, R., et al., *TAPPI J.* 17(7): 395(2018). https://doi.org/10.32964/TJ17.07.395.

30. Linhart, F., Horn, D., Eisenlauer, J., et al., *Wochenbl. Papierfabr.* 115(8): 331(1987).

31. Rao, P.D., Bousfield, D.W., and Tripp, C.P., *Cellulose* 29(9): 4919(2022). https://doi.org/10.1007/s10570-022-04592-9.

32. Li, L., Collis, A., and Pelton, R., *J. Pulp Pap. Sci.* 28(8): 267(2002).

33. Hubbe, M.A. and Gill, R.A., *BioResources* 11(1): 2886(2016). https://doi.org/10.15376/biores.11.1.2886-2963.

34. Hubbe, M.A. and Rojas, O.J., *BioResources* 3(4): 1419(2008). https://doi.org/10.15376/biores.3.2.295-296.