Colloid chemical aspects of paper formation in the presence of nanofibrillated cellulose and cationic starch

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ABSTRACT: A series of experimental tests were carried out to examine colloidal-scale consequences of optionally treating nanofibrillated cellulose (NFC) with cationic starches of different charge density and dosage (0.5% or 2.0% by weight), adding that material to a furnish prepared from 100% recycled copy paper, and then subjecting the mixture to very different levels of hydrodynamic shear. Tests included optical microscopy, sediment volume tests, sediment velocity tests, and "percent fines" assessment by means of a fiber quality analyzer (FQA). In addition, the zeta potential and charge demand of the studied materials were evaluated.

Optical imaging revealed that cationic starch treatment of the NFC tended to agglomerate it into multiparticle clusters, which sometimes could be mostly redispersed by hydrodynamic shear. Subsequent addition of the starch-treated NFC to the default furnish resulted in much of the colloidal material becoming attached to fibers. Subsequent shearing of the mixtures was at least partly effective in separating the clusters of NFC from the fiber surface, resulting in essentially a two-component mixture. Multiparticle NFC clusters coexisted with the fiber suspension, sometimes attached and sometimes not, depending on the details of treatments.

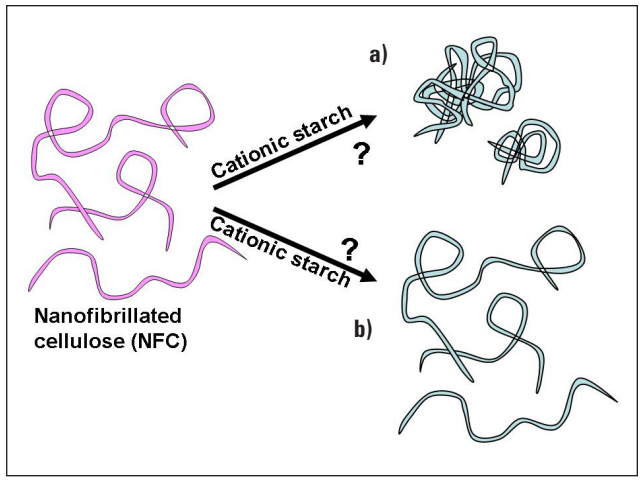
Sediment volume tests showed that systems containing cationic starch-treated NFC tended to have a higher density after settling in comparison to untreated NFC; these findings are consistent with the cationic starch acting as a stabilizer on the solid surfaces, allowing them to slide past each other during the settling process. Application of intense hydrodynamic shear tended to result in denser sediment. Results of tests with the sediment velocity measurement and the FQA percent fines assessment did not correlate well with changes in test conditions considered in this study.

Application: This article describes laboratory tests that can be used to better understand what is happening at a submicroscopic scale when nanocellulose is mixed with cationic starch, as well as other wet-end additives and papermaking furnish, and then subjected to various hydrodynamic shear conditions. Information about colloidal interactions can be helpful for product development and for troubleshooting.

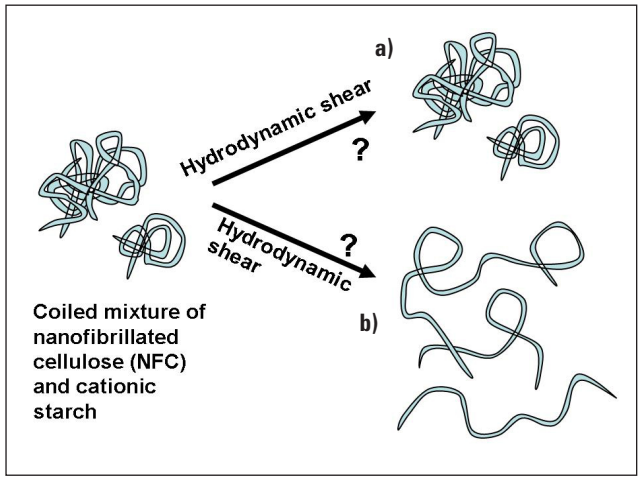
Important aspects of the papermaking process can be understood by focusing on what happens in a size range from about 0.1 to about 10 µm, i.e., the colloidal size range [1]. These dimensions are very common in papermaking systems when one considers the widths of fibrils, lengths of nanocellulose particles, diameters of filler particles, and sizes of many emulsified additives. The hypothesis underlying this work is that colloidal forces – especially electrostatic forces – can help to explain the influence of such additives as cationic starch and nanofibrillated cellulose (NFC) on papermaking operations, including retention, drainage rates, and product uniformity.

In a previous article in this series [2], it was shown that variations in the levels of cationic starch, the type of NFC (either the default freeze-dried NFC or TEMPO-oxidized NFC), and cationic polyacrylamide retention aid (cPAM) had significant effects on such outcomes as fine-particle retention, the rates of dewatering, and paper properties. It was further shown that the results could be shifted by applying different levels of hydrodynamic shear to the suspension before sheet formation.

As a possible way to interpret such effects, **Fig. 1** and **Fig. 2** present a series of hypothetical outcomes when a suspension of NFC (or perhaps, alternatively, macroscopic cellulose fibers) is treated with a chemical flocculant, such as cationic starch (Fig. 1), and subsequent exposure of the flocculant-treated suspension with hydrodynamic shear (Fig. 2). In Fig. 1, the research question is whether or not the polymeric additive causes the suspended fibrillar material to ball up or otherwise change its average shape in the suspension (option A). In these figures, a red or pink coloration implies a net negative charge of a surface, whereas a blue coloration implies a net positive charge. Such effects might be predicted based on bridging or charged-patch interactions of the cationic polymer additives with the generally negative cellulosic surfaces [3]. Alternatively, especially



1. Two possible idealized outcomes when nanofibrillated cellulose (NFC) is treated with a solution of cationic starch. Note that the pink color (left) indicates a weakly negative charge associated with the default NFC used in this work, whereas a light blue color indicates a net weakly positive charge at the surface after the NFC has been added with a sufficient amount of medium-charge cationic starch.



2. Two possible outcomes of application of high levels of hydrodynamic shear.

if the polymer adsorbs in such a way as to stabilize the particles in suspension, the fibrillar material would be expected to remain extended, as in outcome (b).

Figure 2 asks a further research question about what happens if the balled-up material, outcome (a) in Fig. 1, is exposed to different levels of hydrodynamic shear. It is reasonable to expect that intense shearing ought to be able to overcome the polymer bridging connections within the balled-up entity, thereby restoring its stretched-out format. A reason to possibly doubt such a scenario is that shear flow might merely rotate a droplet or cluster of material [4,5] rather than tearing it apart. Extensional flow tends to disperse the material by a mechanism that differs from shear flow [6,7], though studies of such issues have seldom considered submicroscopic fibrillar material or clusters. Switzer and Klingenberg [8] observed that whereas shear flow was able to disperse macroscopic cellulose fibers from each other, extensional flow was initially more effective. A further reason for doubt is the small size of the materials involved, especially when considering NFC. It has been shown, for instance, that hydrodynamic shear can have great difficulty in separating very small particles from solid surfaces [9].

With a goal of probing colloidal effects in the same kinds of papermaking systems as was considered by Hamm et al. [2], a set of experimental assays were carried out in this work. These included a sediment volume test, a sedimentation velocity test, a "percent fines" test, and imaging by optical microscopy. In addition, the electrical charge characteristics of fibers and colloidal suspensions were evaluated by means of polyelectrolyte titrations [10,11] and fiber-pad streaming potential tests [12,13].

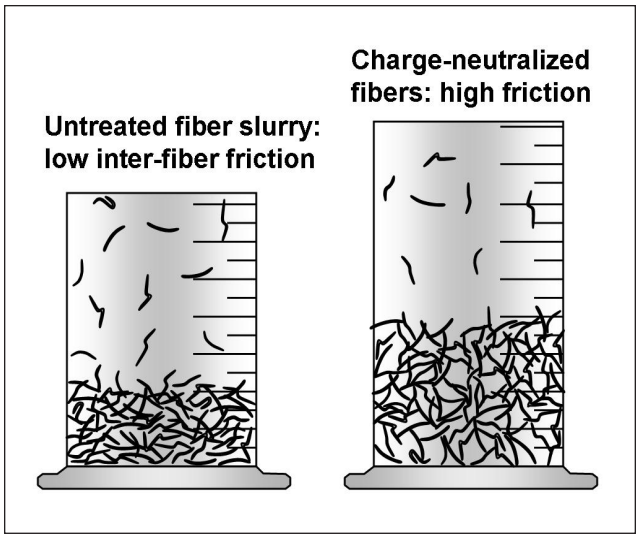
The goal of the sediment volume test is to detect changes in the frictional contacts between particle or fibrillar entities in the mixture. The method has been used since as early as 1959 [14], and it has been used repeatedly more recently [15-18]. As depicted in **Fig. 3**, the procedure can be conveniently conducted by placing an initially well-dispersed suspension within a graduated cylinder. After waiting for a set time, such as an hour or a day, one observes the height of the sediment. The usual assumption is that sticking interactions between the solid surfaces, upon their initial contact, will prevent them from sliding relative to each other, thereby resisting densification of the sediment. To the best of the authors' knowledge, this kind of analysis has not yet been done for systems containing NFC.

It is well known that the settling rate of perfect spheres in a liquid, at low Reynolds numbers, can be accurately predicted by knowing the radius and the density of the sphere and the suspending fluid [19]. This is done by applying Stokes' law, which can be expressed as follows:

$$v = (2/9)\,[\rho_p - \rho_f]\,g\,R^2 / \mu$$

In this equation, v is the velocity; ρ_p is the density of the particle; ρ_f is the density of the fluid; g is the acceleration of gravity; R is the particle radius, and μ is the dynamic viscosity of the fluid.

It is proposed here that the Stokes equation could be applied, in an approximate way, to characterize the behavior of agglomerates of particles or fibrous entities. Two factors in the equation need to be considered. In place of the radius of a spherical particle, one might substitute the average or effective radius of the agglomerate. In place of the particle density, one might substitute an effective density, noting that much of the volume within the agglomerate will be filled by the fluid phase, which will affect the overall density. In addition, it has been shown that a cluster of small particles settles more slowly than the Stokes equation would suggest, presumably due to the greater surface area,



3. Schematic illustration of the effect of colloidally stable conditions (left) vs. conditions leading to sticking collisions (right) on the volume of sediment after a set period of settling.

which contributes frictional resistance to passage through the fluid [20]. In practice, it is likely that neither the effective radius nor the effective density of the agglomerates will be known. Rather, the observed differences in settling rates can be expected to provide a composite effect involving both density and radius.

Optical microscopy was chosen for this project as the means to find out about the shapes of NFC, in combination with other materials and additives, as they are affected by their interactions with each other and as a consequence of hydrodynamic shear. Although optical microscopy does not have as high resolution as scanning electron microscopy, it has the advantage of being able to examine aqueous systems. In addition, even though the term NFC suggests "nano" sizes that would be below the resolution capability of optical microscopy, the materials used in the present work, especially when in an agglomerated state, require that objects of up to millimeter scale need to be shown in images. Another advantage is that the crystalline regions of natural cellulose, even when highly fibrillated, are optically polarized; thus, by using a microscope with crossed polarized imaging capability, enhanced images can be obtained [21,22]. Key questions to be addressed are: (a) to what extent different chemical additives act to contract NFC into individual balls or clusters; and (b) whether such balls or clusters, once formed, can be dispersed by different levels of hydrodynamic shear. Due to time constraints, as well as the exploratory nature of the present study, there will be a need for more replication in follow-up research.

The fiber quality analyzer (FQA), which is based on optical microscopy, was tested in this work as a possible supplementary way to obtain or summarize the information from microscopy. It is worth noting that the FQA was not designed or intended for such usage. However, due to the presence of the equipment in many paper industry laboratories, it has been used by researchers studying NFC. In particular, the percent fines output has been used as a way to quantify the degree of completion of NFC preparation [23,24]. Whether the method will be useful for examination of effects due to various papermaking additives, with or without application of hydrodynamic shear, was determined in the work to be described.

EXPERIMENTAL

Chemicals and materials

The chemicals used in this experimental work were in general the same as those listed by Hamm et al. [2]. These included medium-charge density cationic starch with nominal degree of substitution of around 0.03 (source not disclosed) and Chargemaster L340 high-charge density cationic starch (Grain Processing Corp.; Muscatine, IA, USA) with a degree of substitution around 0.20. Both of these products were corn starch in which the molecular mass had not been intentionally decreased. The cationic acrylamide copolymer retention aid (cPAM), in dry-bead form, was a product of American Cyanamid (Wayne, NJ, USA). Its nominal charge density is 10%, and the molecular mass is several million Daltons. The cPAM was diluted to 0.1% solids with deionized (DI) water and stirred for an hour before use.

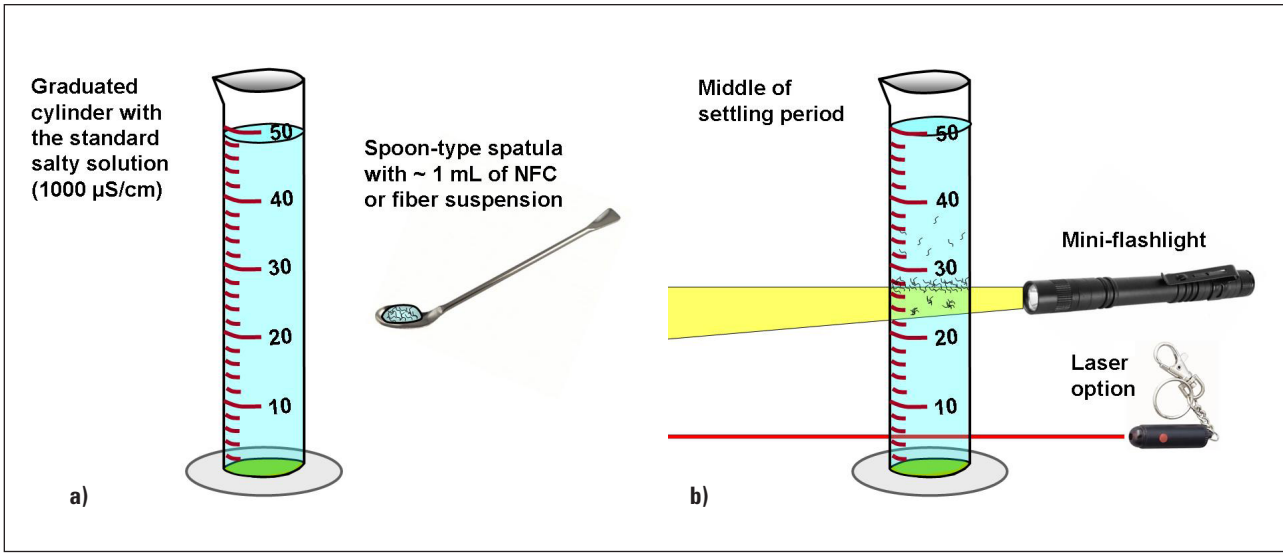
Two types of dry nanofibrillated cellulose (NFC) were from the University of Maine (Orono, ME, USA), namely the default freeze-dried NFC and a TEMPO-oxidized version (TONFC). Suspensions were prepared at a solids content of 0.5% and an electrical conductivity of 1 mS/cm, which was achieved by adding sodium sulfate (Na_2SO_4).

Pulp preparation

As in the work of Hamm et al. [2], the fiber was obtained by repulping Boise Aspen recycled multi-use paper (Boise Paper; Boise, ID, USA), with 100% recovered fiber content and 22.7% of calcium carbonate ($CaCO_3$) filler by dry mass [25]. This was prepared at 0.5% consistency with an electrical conductivity of 1000 µS/cm with the addition of Na_2SO_4 solution. The pH was approximately 8.2.

Evaluation of zeta potential

The zeta (ζ) potential at the surfaces of the wet cellulosic materials was determined by fiber-pad streaming potential measurements [25]. Briefly stated, house vacuum (approximately 95 kPa) was applied to draw 0.5% solids fiber suspensions toward a 100-mesh screen. The voltage difference was measured by means of metal probes (welding wire) on the opposing sides of the screen, with a pad of fibers on it. The welding wire was insulated using tight-fitting plastic tubing, which was sealed with waterproof glue so as to expose just the sections on the opposite sides of the screen. The difference in the potential, when comparing the vacuum-applied value with the non-pressurized value, was in-



4. A 1 mL fiber suspension is added to the standard saline solution, and its descent is tracked.

serted into the Helmholtz-Smoluchowski equation [26,27]:

$$\zeta = 4\pi \Delta E \eta\lambda / (\Delta P \varepsilon)$$

where ΔE is the measured difference in voltage between the probes, η is the viscosity, λ is the electrical conductivity, ΔP is the applied vacuum, and ε is the dielectric constant.

Charge demand titrations

Cationic or anionic demand information was obtained by titration with either poly(diallyldimethylammonium chloride), i.e., poly-DADMAC, or poly(vinyl sulfate) as the titrants. The endpoints were detected using an Emtec CAS touch! (Emtech Electronic; Leipzig, Germany) streaming current detector. The amount of titrant, together with its molarity, at the point of zero output signal, were used to calculate the charge demand values in micro- or milliequivalents of charge per dry gram of solids in a known volume (10 mL) of suspension.

Sediment volume determination

Sediment volume was determined visually. For each tested condition, the fiber suspension was added at 0.1%–0.2% consistency by mass to a graduated cylinder of 1000 µS/cm³ Na_2SO_4 solution, for a total volume of 50 mL (filling up a graduated cylinder). The suspensions were allowed to sit for periods of 1 h, 24 h, and sometimes for 1 week. Over this period, both quantitative and qualitative observations were made. Based on the results, a 24-h period was selected as providing the clearest differentiation based on different conditions of preparation.

Sedimentation velocity determination

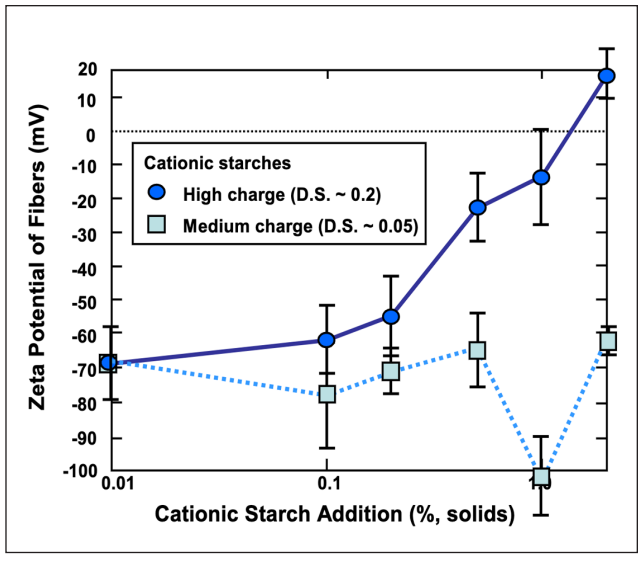
Sedimentation velocity was determined by first filling a set of 50 mL graduated cylinders with 1000 µS/cm³ Na_2SO_4 solution. For each tested condition, approximately 1 mL of suspension (to be described) was added to the top of the filled cylinder. The descent of the solids (either individual particles or agglomerates) was tracked with a narrow-beamed flashlight, as illustrated in **Fig. 4**. A stopwatch was used to determine the elapsed time for the main portion of the suspended material to reach the bottom of the cylinder. A laser beam, as depicted in the figure, was found to give essentially the same information.

Fines determination using the fiber quality analyzer

An FQA device from OpTest Equipment (Port Hawkesbury, ON, Canada) was utilized to provide supplementary quantification of the percent fines content in the prepared suspensions of nanocellulose or fibers, as will be described. A very dilute solution of the suspension in 600 mL DI water was used. The amount of suspension added to the DI water varied, but generally it was 1 mL or less. The FQA automatically stops at a fines count of 4000 and returns percent fines as both arithmetic and weighted means. The default setting of the FQA defines fines as having a length of 0.2 mm or less.

Optical microscopy with polarized light options

A Nikon Eclipse E200 POL polarizing microscope (Nikon, Tokyo) was used to visually observe flocculation in the prepared fiber suspensions. Different samples were observed at 40x, 200x, and 400x magnifications. Most observations were carried out with the standard settings of the compound optical microscope. It uses a halogen lamp to illuminate the samples. The brightness and condenser diaphragm were adjusted to allow for the best view of each individual sample. The specific objectives used were the following: CFI Achro P 4X, CFI Achro LWD P 20X, and CFI Achro P 40X. There were not any additional filters/plates/etc. added for the majority of images.



5. The effect of cationic starch addition on zeta potential. Adding high-charge starch increased the zeta potential. The data for adding medium-charge starch did not show a significant trend. Error bars indicate standard deviations (D.S.: degree of substitution).

Some samples were observed using polarized light and a full-wave retardation plate. Only one drop of diluted sample was viewed per testing condition, so making definitive conclusions based on the microscopy observations is difficult. Micrographs were instead used to support conclusions visually, based on other experimental results.

RESULTS

Zeta potential results

As shown in **Fig. 5**, before adding the cationic starch, the zeta potential of the default fiber furnish was negative. This is consistent with what is expected for untreated papermaking fibers. It should be noted that the fibers and filler used in this work were from recycled paper, which is expected to contain not only bleached kraft fibers, but also calcium carbonate filler, various wet-end chemicals, and size press starch that were added during previous cycles of production. Thus, the observed negative zeta potential can be viewed as a combined effect of different substances in the furnish.

The high-charge cationic starch clearly was able to reverse the negative zeta potential of the furnish when added at approximately 1%–2% based on solids. By contrast, the medium-charge cationic starch did not have a significant effect on the measured zeta potential within the range of addition considered in this work. There was also some scatter in the data. An explanation for these findings, in the case of the medium-charge density cationic starch, lies in the mesoporous nature of bleached kraft fibers, as shown by Hubbe et al. [28]. As found in the cited work, ordinary measurements of fiber zeta potential, using the streaming potential method, actually report a composite result from two different regions, namely the fiber surface and also the mesoporous interior of those fibers. Because cationic polymers are mainly on the outside of the fibers, at least initially, the measured streaming potential (and calculated zeta potential) can be negative even when the charge at the fiber surfaces has a net positive charge.

Charge demand properties

Table I compares the charge demand values of solutions of medium-charge cationic starch, high-charge cationic starch, and cPAM retention aid. The high-charge cationic starch had a higher titratable charge than the medium-charge cationic starch. This is consistent with expectations. However, the ratio of the mean values (200/50 = 4) was not as high as would be estimated by the nominal degree of substitution values provided by the suppliers (0.20/0.03 = 6.7). The difference is likely explainable by the expected non-stoichiometric interactions with the titrant, especially when evaluating low-charge density specimens and when carrying out such measurements in the presence of salt ions [29]. Out of the three cationic polymers, the cPAM had the highest positive charge demand on a weight basis.

Table II shows corresponding results for when the same three polymer solutions were added to portions of the default fiber suspension, followed by filtration through a mesh screen and titration of the filtrate. As in Table I, all of the mixtures required the addition of anionic titrant to reach the neutral end point, thus indicating a net positive charge condition. In each case, the act of mixing the polymer solution with the stock had the effect of decreasing the remaining positive charge. This is consistent with the negative charge of the default furnish, as shown previously by means of the streaming potential tests. However, the specimens were shown to be in the same order of charge density as when they were evaluated directly in DI water (Table I).

	Mean	Standard Deviation
Medium-charge cationic starch	50	5
High-charge cationic starch	200	82
Cationic polyacrylamide (cPAM) retention aid	1200	225

I. Anionic demand of cationic polymers in water (μeq/g solids).

	Mean	Standard Deviation
Medium-charge cationic starch	6	20
High-charge cationic starch	19	58
Cationic polyacrylamide (cPAM) retention aid	648	262

II. Anionic demand of cationic polymers (1%) mixed with furnish (μeq/g solids).

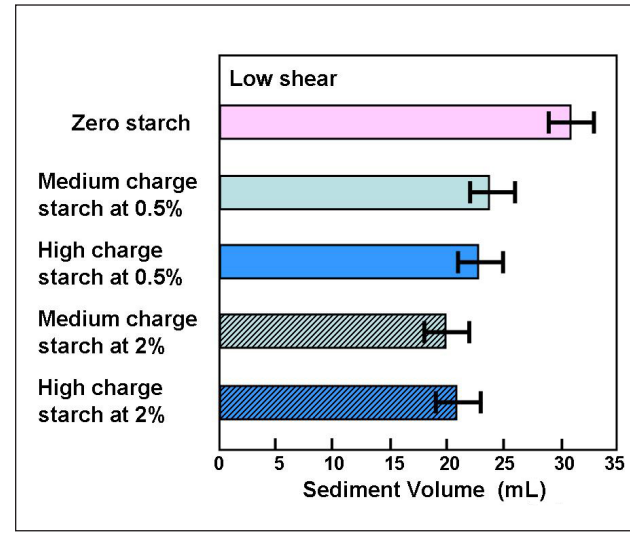
	Low Shear	Medium Shear	High Shear
No starch	32	30	18
0.5% medium-charge cationic starch	25	30	23
2.5% medium-charge cationic starch	30	35	30
0.5% high-charge cationic starch	33	27	23
2.5% high-charge cationic starch	33	–	25

III. Sediment volume (mL) of NFC suspensions after 24 h settling with different levels of cationic starch addition and shearing.

Sediment volume results

The addition of cationic starch to the default NFC tended to decrease the sediment volume. Higher levels of starch addition gave a larger effect, on average, but that was not observed to be statistically significant, as shown in **Fig. 6**. A decreased sediment volume can be taken as evidence of decreased friction between the fibers, which allows the fibers to pack closer together when settling. Thus, rather than causing the fibers to stick to each other on contact, the results suggest a net effect of the cationic starch was to prevent close approach of the fiber surfaces at a nanometer scale, thus helping the surfaces to slide past each other. In other words, the results are the opposite of what had been hypothesized in Fig. 3. The cationic starch, rather than acting as a coagulant or bridging agent, instead contributed to colloidal stability, presumably by providing repulsion and keeping the surfaces from rubbing against each other [3].

Table III shows related findings, now focusing on effects of different levels of hydrodynamic shear, which were applied following the treatments of NFC with cationic starch. As shown, application of the highest level of shear (using a blender) generally gave the lowest values of sediment volume. This is consistent with a breakage of any initial bridging by cationic starch molecules of adjacent cellulose surfaces. Once the starch is more evenly spread on all the surfaces, especially at a high addition level of the starch, then it is more likely that the positive charges of the adsorbed starch molecules will cause the adjacent surfaces to repel each other at nanometer distances. This would allow the surfaces to slide past each other, giving rise to a denser sediment. It was interesting to note that a medium level of shear gave the highest values of sediment volume

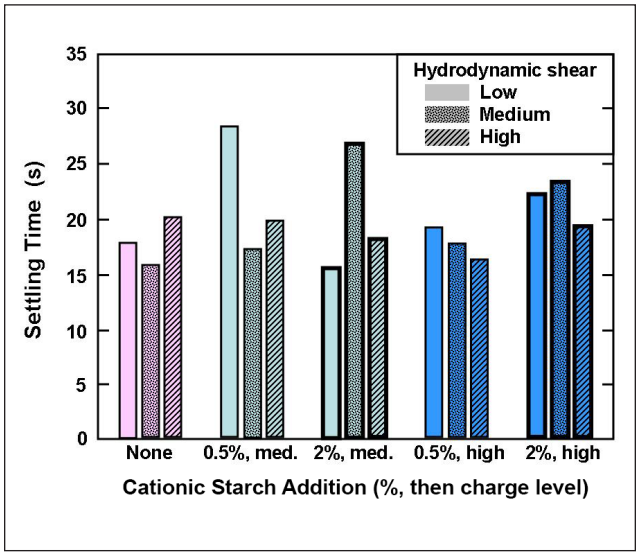


6. The effect of cationic starch addition to default nanofibrillated cellulose (NFC) on sediment volume. Error bars represent 95% confidence intervals for the mean values. The colors suggest trends in system charge, with pink indicating a weak negative surface charge and the depth of blue coloration indicating increasing net positive charge.

for treatments involving the medium-charge cationic starch. The reason is not fully known. It is reasonable to expect there is an optimum level of shear that will facilitate formation of bridging contacts between the surfaces such that some single macromolecules of cationic starch may be simultaneously in contact with two adjacent surfaces.

Sedimentation velocity results

Figure 7 shows related data for sedimentation velocity tests in the case of TEMPO-oxidized NFC. It had been hy-

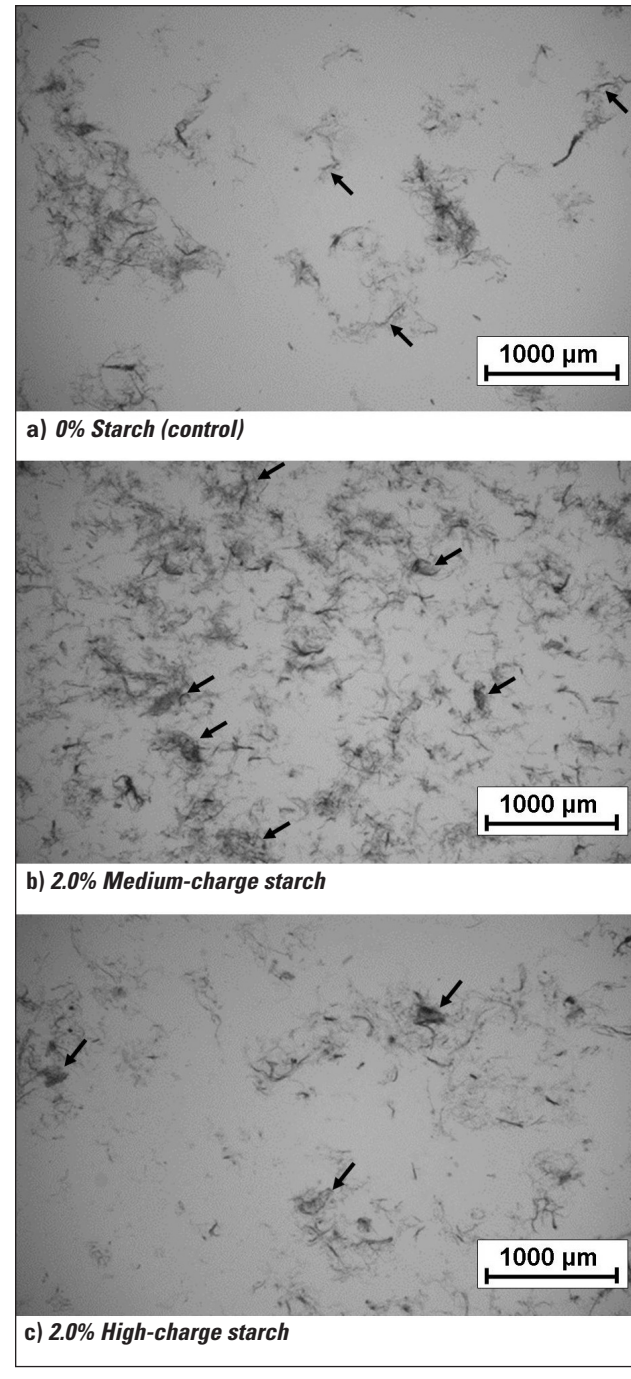


7. The effect of cationic starch addition to TEMPO-oxidized NFC on settling velocity. No significant effect was observed. The colors suggest trends in system charge, with pink indicating a weak negative surface charge and the depth of blue coloration indicating increasing net positive charge.

pothesized that results of such tests could be interpreted based on the Stokes equation. If one were to assume a relatively constant apparent density of the solids, then a higher sediment velocity would be indicative of a larger size of flocculated material. Such an effect was apparent in many cases when the mixture was subjected to the highest level of hydrodynamic shear. However, the breakup of flocs would be expected to yield smaller particles and generally a higher settling time, which was the opposite of what was observed. There was no clear effect when cationic starch was added to the furnish. Charge densities or levels also did not have any consistent effect within the trials with starch addition. Tests carried out with the default NFC likewise did not show significant effects on sedimentation velocity. The lack of correlation between the settling velocity results and changes in experimental conditions might be due to known problems involving the usage of the Stokes equation in its original form. For instance, water is able to flow through clusters of particles, and this has been shown to have major consequences [30,31].

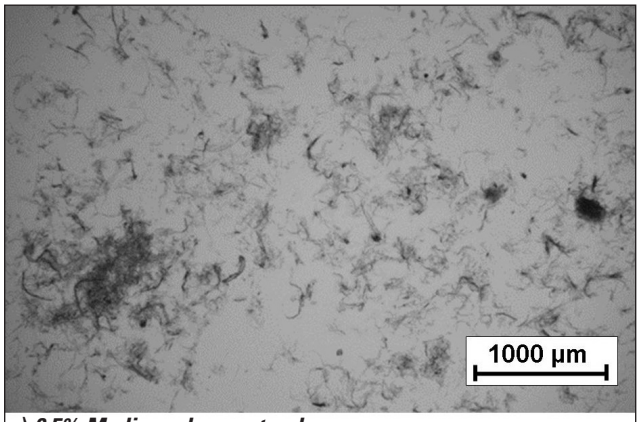
Microscopic analysis

Figure 8 shows optical microscopy images of suspensions of the NFC either in the default Na_2SO_4 solution alone or after further treatment with cationic starch of the indicated charge density at the 2% level (a high dosage). Mixtures were subjected to only gentle stirring after the addition of the cationic starch solutions. As shown in Fig. 8a, the untreated NFC mostly was present in loosely entangled flocs. Some denser areas (see arrows in the figure) suggest the appearance of strands of multiple NFC particles twisted together, which might have been a result of mixing action

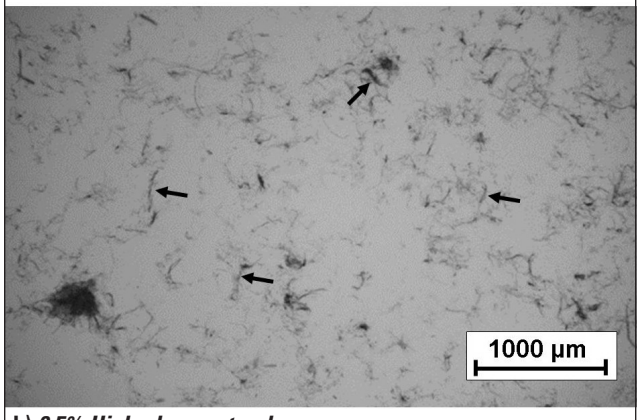


8. The effect of 2.0% cationic charge density on flocculation in the case of the default NFC. More flocculation was observed in the suspensions with medium-charge starch, but it is unclear from these results whether that was significant. The control showed fewer but larger flocs.

either before or after the starch addition. As shown in Fig. 8b, the addition of medium-cationic starch appeared to give a greater extent of flocculation such that the flocculated structures appeared darker in the image (see arrows in the figure). This is consistent with a bridging action of the medium-density cationic starch, especially in the absence of substantial hydrodynamic shear. Contrasting results were

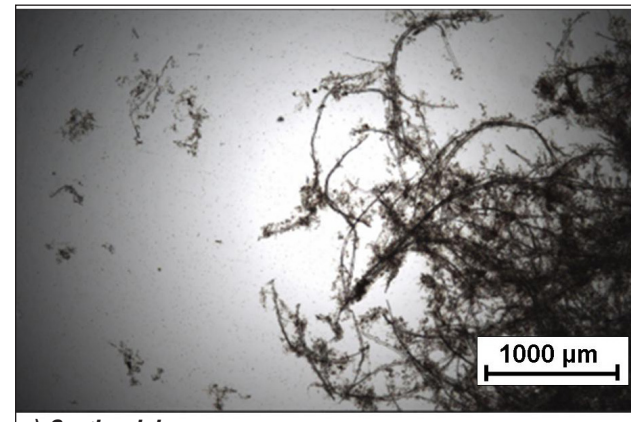


a) *0.5% Medium-charge starch*

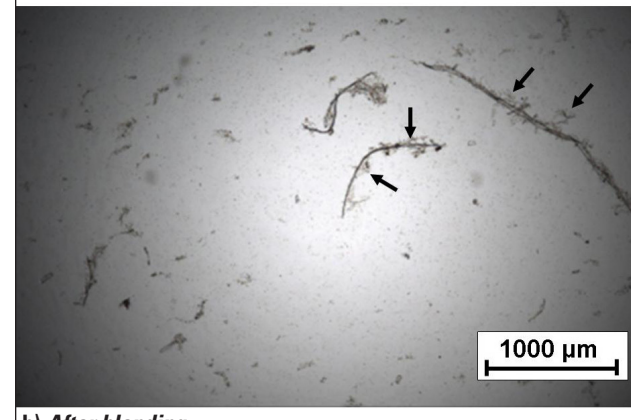


b) *0.5% High-charge starch*

9. The effect of 0.5% low or high cationic charge density starch on flocculation in the case of the default NFC.



a) *Gentle mixing*



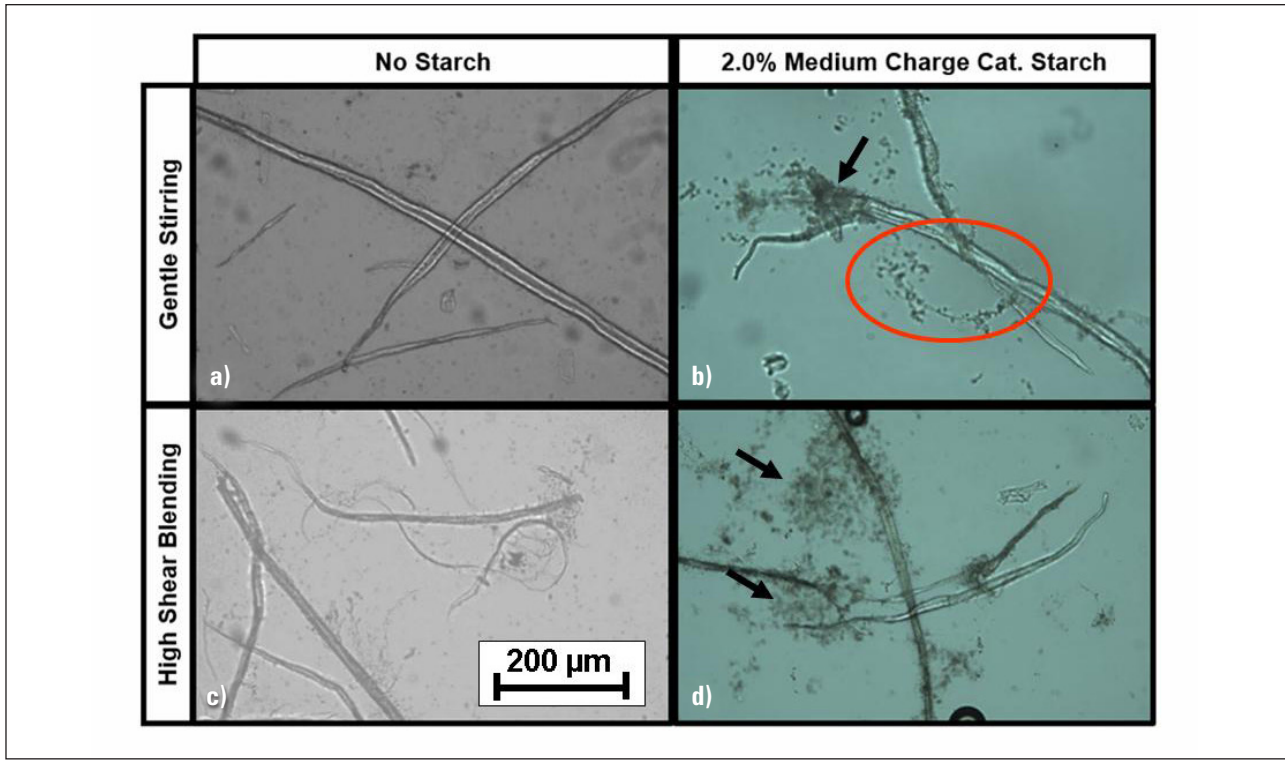
b) *After blending*

10. Optical images of a suspension with 2.0% medium-charge cationic starch dosage onto freeze-dried NFC, which was blended, then mixed with default fiber suspension (a) vs. the same preparation that was also subjected to a final high-shear treatment in a blender (b), both at 40x magnification.

apparent after treatment with high-charge density cationic starch, still at the 2% level (Fig. 8c). This image appears to show two main populations. There were some distinct flocs present (see arrows in the figure). But on closer inspection, a majority of the NFC appeared to be well dispersed and therefore less distinct in the image. Such a combination of appearances suggests that while there was some bridging action of the high-charge cationic starch, much of the effect could be described as charge-stabilization of the suspension due to an apparent excess of adsorbed high-charged cationic starch.

Figure 9 shows images from related systems, but at the lower treatment level of 0.5% based on the mass of the default freeze-dried NFC. To put things into context, the 0.5% treatment level was far below the dosage required to reverse the sign of the zeta potential for the high-charge starch treatment (as was shown in Fig. 5). However, in this case the solids were NFC, which has a much higher surface area than the default furnish considered in Fig. 5. Thus, a charge-stabilization mechanism would not be anticipated. However, differences between the two images showed the same general trend as those shown in the previous figure for the 2% treatment level. Thus, the medium-charge cationic starch at the 0.5% level appeared to increase the flocculation level of the NFC suspension. The high-charged cationic starch once again gave rise to a mixed population that included both some relatively dense flocs, contrasting with a major portion of the NFC that appeared well dispersed, with some evidence of twisted strands (see arrows in the figure), as noted earlier for the untreated NFC suspension (Fig. 9a).

Shear level had a more pronounced effect on flocculation, as shown in **Fig. 10**. In this series, a suspension of default NFC was first treated with medium-charge cationic starch at the 2.0% treatment level. The starch-treated NFC was subjected to intense hydrodynamic shear in a blender. Then, the NFC mixture was added with stirring to the default fiber suspension. Figure 10a shows the appearance of that combination of ingredients after gentle mixing, whereas Fig. 10b shows a corresponding specimen after 30 s of high shear in the blender. The specimen that received the latter blending, after combining the treated NFC with the furnish, showed a high degree of redispersal of the fibers from each other. Thus, after the shear application, there



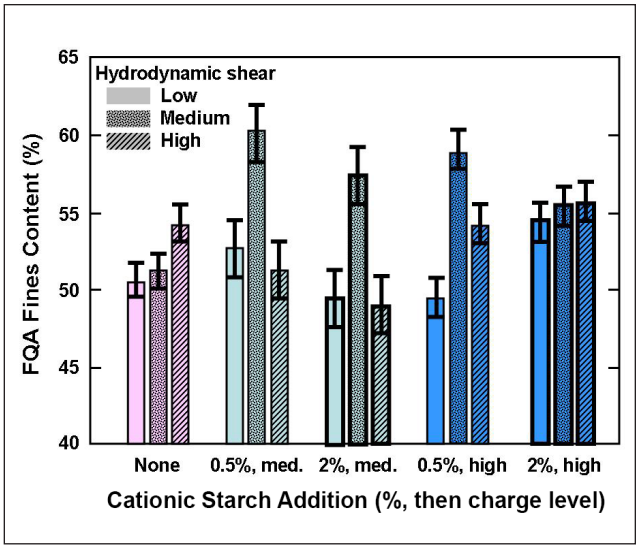
11. Optical images of a suspension with zero or 2.0% medium-charge cationic starch dosage onto freeze-dried NFC, which was blended, mixed with default fiber suspension, and gently stirred or subjected to high shear in a blender: (a) freeze-dried NFC untreated and subjected to blending, and then added to the default fiber suspension and gently stirred before imaging; (b) NFC treated at the 2.0% level of medium-charge cationic starch, then blended, and then added to the default fiber suspension and gently stirred before imaging; (c) untreated NFC subjected to blending, and then added to the default fiber suspension and sheared in a blender before imaging; and (d) NFC treated at the 2.0% level of medium-charge cationic starch, then blended, and then added to the default fiber suspension and blended before imaging.

was a higher amount of fine fibrillated matter resembling nanocellulose spread out and relatively well dispersed. This is consistent with the expectation that higher shear levels will break up flocs. In addition, there were clusters of fine matter, presumably NFC, still attached to fiber surfaces (see arrows in Fig. 10b).

Figure 11 shows results from similar experiments, except that highly anionic TONFC was used. The cationic starch treatment was 2.0% dosage, when used. The figure compares two levels of hydrodynamic shear, namely gentle stirring and blending. The images on the left (Fig. 11a and Fig. 11c) correspond to untreated TONFC, whereas those on the right (Fig. 11b and Fig. 11d) were treated with medium-charge density cationic starch. On the vertical axis of the figure (Fig. 11a and Fig. 11b), the top images correspond to gentle stirring, whereas the bottom images (Fig. 11c and Fig. 11d) are after the suspensions (untreated or treated) had been subjected to intense shearing with a blender. As shown in the absence of starch treatment, the nanocellulose, as initially prepared, showed some tendency of loose association, and it was generally not adhering to the surfaces of the cellulosic fibers, which appear much larger in the images. When the untreated suspension was subjected to high shear in a blender, the nanocellulose portion of the solids appeared to become more evenly dispersed and less self-associated. Considering the gentle stirring conditions at the top of the figure, the addition of cationic starch at the 2.0% level caused the TONFC to become clumped together and also to become associated with fiber surfaces (see arrow in Fig. 11b). As in the early research by Haslam and Steele [32], some of the fine matter was preferentially attached to fibrils extending outwards from the fibers (see circled area in Fig. 11b). Application of high hydrodynamic shear to the starch-treated mixture made the flocs of TONFC less dense, but it did not fully redisperse them, and much of the fine solids remained associated with fiber surfaces (see arrows in Fig. 11d). An image of starch-treated TONFC in the default fiber furnish that had been subjected to an intermediate shear level (impeller stirring) was generally intermediate between the two images shown in Fig. 11b and Fig. 11d.

Fines percentage based on the fiber quality analyzer

The FQA device was evaluated in this work as a potential supplement for the microscopic work just discussed. The goal was to find out whether the percent fines output from the FQA would correlate with other findings and whether



12. The effect of cationic starch addition on fines content, as reported by the fiber quality analyzer (FQA), in the case of the default NFC. Error bars represent 95% confidence intervals for the mean values. The colors suggest trends in system charge, with pink indicating a weak negative surface charge and the depth of blue coloration indicating increasing net positive charge.

it could be used as a reliable measure related to the state of agglomeration or dispersion in papermaking systems containing highly fibrillated cellulosic material. Notably, the FQA device uses digital images as a means of quantifying the fines content.

As shown in **Fig. 12**, an intermediate shear level often increased the fines detected by the FQA in systems treated with cationic starch. However, there was no well-defined trend. The difficulty in interpreting the FQA results are tentatively attributed to the fact that there is both a lower size limit and an upper size limit of image features that would be counted as fines by the FQA system. The default settings were used, such that 0.2 mm was the maximum dimension for an object to be identified as a fine. But the lower limit was hard to define, since it was related to the optical resolving power of the equipment. As indicated in some of the microscopic images, well-dispersed NFC tended to become indistinct in the photographic images, and a similar effect might be expected for the electronic images captured during the FQA testing.

DISCUSSION

Several hypotheses were mentioned in the introduction regarding the possible clumping, and then the possible redispersion, of NFC suspensions as a result of adding cationic starch, followed by different levels of hydrodynamic shear. Though some of the collected observations in this work supported each of the hypotheses described in the introduction, there also was evidence of effects of cationic starch treatment and hydrodynamic shear on whether or not NFC (or clumps of NFC) were bound to the fiber surfaces. Another issue that emerged based on the microscopic observations was that the most evident clumping of NFC, as a result of interactions with cationic starch, involved multiparticle NFC clumps. Prior work has shown that freely suspended fines, not attached to fiber surfaces, are prone to interference with dewatering of fiber mats [33]. Therefore, it is an important finding of the present work that fiber suspensions that include cationic starch-pretreated NFC, with certain levels of hydrodynamic shear, can result in multiparticle NFC clumps, which may be either attached or not attached to fibers in different cases.

High levels of hydrodynamic shear appeared to be effective in dispersing systems with ordinary NFC (having a low level of negative charge at its surface) after treatment with cationic starch. In the case of TEMPO-oxidized NFC, the results were mixed, suggesting persistence of some clusters of the highly fibrillated material even after very strong shearing. Such behavior is consistent with an expected strong electrostatic interaction between the cellulosic material and the cationic starch. On the other hand, in cases where the hydrodynamic shear was found to be effective in redispersing the NFC (especially the combination of medium-charge cationic starch and default NFC), the cationic starch might have served as a stabilizing agent in the final mixture. In other words, uniformly distributed cationic starch on all the surfaces may have provided a charge barrier and a steric barrier opposing sticking collisions between the solid surfaces.

Results of the present work involving colloidal interactions can be useful in understanding some of the findings reported by Hamm et al. [2]. For example, the cited work showed that an intermediate level of hydrodynamic shear in systems containing TONFC, followed by cationic retention aid (cPAM), gave by far the slowest vacuum drainage. Such behavior suggests that the shear was enough to detach much of the highly fibrillated material from the fiber surfaces, such that it was effective in plugging drainage channels within the wet mat of paper [33]. The fact that the drainage penalty was reduced when the system was sheared in a blender suggests that a certain size of agglomerates that include NFC may be especially effective in impeding dewatering. This suggestion merits further study.

None of the hypotheses already mentioned in this article said anything specific about what is happening to the mineral component of the furnish, i.e., the $CaCO_3$, that was present in the recycled copy paper. If one makes the assumption that much of the $CaCO_3$, would tend to associate itself with the cationic starch-NFC mixture, then the present results can help to explain some of the first-pass retention results presented by Hamm et al. [2]. In particular, increasing hydrodynamic shear resulted in increased turbidity, meaning that progressively less light-scattering material, especially the $CaCO_3$ particles, were being retained

on the fibers. Due to their size being near to the wavelengths of visible light, the $CaCO_3$ particles play a disproportionate effect in the scattering of light. At a medium level of shear of the final mixture, the high-charge cationic starch gave much higher turbidity than the medium cationic starch. This is consistent with a charge reversal situation, which would be expected to lead to unattached fine matter in the furnish.

A puzzling issue that was not well explained in the article by Hamm et al. [2] is why the tensile strength appeared to be unaffected by the level of final shear treatment. This was despite the fact that increasing hydrodynamic shear was shown to reduce the amount of filler present in the resulting handsheets, as well as make the paper more uniform. Based on the present results, it is possible to offer another hypothesis to explain those results. It is proposed here that application of hydrodynamic shear to a mixture of cationic starch-treated NFC and fibers has the potential to convert the system into a mixture of two components that do not become well integrated with each other during the paper forming process. The present results show that the mixture of nanocellulose and cationic starch can be formed into clusters, which can vary in terms of density, and which can become detached from fiber surfaces with increasing levels of hydrodynamic shear. The fact that many of the NFC-rich clusters persisted even after exposure to intense hydrodynamic shear is consistent with the small size of those clusters, making them somewhat difficult to detach from the fiber surface, but even more difficult to be dispersed from each other at a given level of hydrodynamic shear [9].

CONCLUSIONS

Meaningful differences, depending on changes in NFC type, cationic starch type and treatment level on the NFC, and application of hydrodynamic shear were detected or quantified in this work by various experimental methods. Optical microscopy was found to be an effective way to reveal information regarding the state of clumping, clump density, and the extent of redispersal by hydrodynamic shear of the fine matter in the fiber suspensions.

Some important findings of this work were that after NFC had been treated with cationic starch at the 0.5% or 2.0% level based on solids, the material became clustered. Intense shearing with a blender sometimes was able to redisperse such suspensions; for instance, when the NFC was of the ordinary type, having a low absolute value of surface charge. But in other cases, such as when using TEMPO-oxidized NFC, the initial clusters were hard to fully disperse by shear. Initial mixing of cationic starch-treated NFC with stock from repulped 100% recycled copy paper resulted in adsorption of the NFC material to the fiber surfaces; however, subsequent application of shear was able to redisperse some of that material from the fiber surface. The redispersed NFC material in such sheared mixtures with papermaking fibers tended to be self-associated into multiparticle clusters that resisted dispersal by shear.

Sediment volume tests were found to be easy to carry out, and a 24-h period of settling gave a good differentiation, especially when evaluating effects of final shearing. Those results appeared consistent with an expectation that the shear-redispersed suspensions were effectively stabilized by an adsorbed layer of cationic starch, allowing the surfaces to slide past each other and thereby forming a denser sediment.

Two types of tests that did not appear to provide useful information, at least in the context of the systems considered in this work, were sediment velocity and the percent fines value obtained from the FQA device. A likely explanation for the poor explanatory power of the sediment velocity test might be that the Stokes sedimentation equation, which requires the assumption that the system behaves like impermeable spherical solid particles, was a poor fit with the physical situation. A key difference between a fiber or nanofiber cluster and a sphere is that water can flow through and around a cluster of fibers [30,31]. A likely explanation of the poor explanatory power of the percent fines measurements could be related to the fact that the FQA system was not designed to measure stock systems containing nanocellulose. The FQA device attempts to measure fines as the amount of material that is large enough to be distinctly visible in an optical micrograph, but having a maximum length less than 0.2 mm. Some parts of the NFC used in the present work have dimensions that are too small to show up clearly in the FQA's imaging system [34]. In any case, there did not appear to be a good fit between the percent fines measurements and effects of changes in such variables as cationic starch treatments and hydrodynamic shear application. **TJ**

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About this journal

ABOUT THE AUTHORS

We studied this work because some questions remained after the work by Hamm et al. reported in this issue of *TAPPI Journal*. In particular, how did the treatments with cationic starch and hydrodynamic shear affect the shape of the nanocellulose?

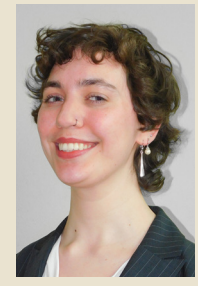
In this work, we performed a series of tests to characterize what happens at the colloidal-size scale when nanofibrillated cellulose is treated with cationic starch and then added to papermaking furnish with optional cationic retention aid and hydrodynamic shear. This had never been done before.

One difficult aspect of this work was that tests using optical microscopy needed input from someone experienced with the method. For that reason, we recruited Taylor Kanipe, one of the authors of this paper, who has been using such microscopy for her Ph.D. thesis work.

We discovered that even if one forms a hypothesis about possible outcomes of experimentation, the actual results can be more complicated in interesting ways. Our most surprising discovery was that the nanocellulose appeared to separately form multiparticle clusters, and once formed, the clusters were difficult to separate again, depending on the details.

The methods used in this work, especially the microscopy, sediment volumes, and zeta potential analysis, can be useful for product development work involving nanocellulose applications in papermaking.

The work described in the work of Hamm et al., as well as the present article (Jones et al.), is not the whole story. The next step is to examine what happens when colloidal silica is added in addition to the nanocellulose and the cationic starch.



Jones

Atree

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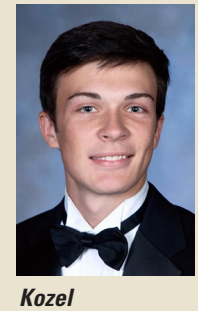

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Kanipe

Hubbe

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