Effects of carboxymethyl starch as a papermaking additive

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ABSTRACT: Carboxymethyl starch (CMS) is a bio-based, anionic polymer that has potential as part of a dry-strength additive program for papermaking. Due to its negative charge, its effects can be expected to depend on its interactions with various cationic agents.

In this work, the effects of CMS were observed following its sequential addition after one of three selected cationic strength agents at different dosage levels. In selected tests, the furnish was pretreated at the 1% level by a dispersant, sodium polyacrylate, which might represent a high level of anionic contaminants in a paper mill system. Laboratory tests were conducted to show the effects on dewatering, fine-particle retention, and flocculation. These tests were supplemented with measurements of charge demand, zeta potential, and handsheet properties. Sequential addition of cationic glyoxylated acrylamide copolymers (gPAM) and CMS were found to strongly promote dewatering. Two gPAM products and a poly(vinylamine) product in sequential addition with CMS were very effective for promoting fine-particle retention. These same sequential treatments of the stock contributed to moderate fiber flocculation, though severe flocculation was caused by further treatment of the furnish with colloidal silica. Handsheet strength results were mixed. In the default recycled copy paper furnish, the average breaking length for the sheets made with cationic additives followed by CMS was not greatly different from the blank condition. Superior strength resulted when the default furnish was treated with a dispersant alone. When the dispersant-contaminated furnish was treated with the same combinations of cationic additives and CMS, the strength returned to the baseline achieved in the absence of the dispersant. The results were discussed in terms of the charged character of the different additives and their interactions not only with the fiber surfaces but also with each other.

Application: In an effort to achieve required strength properties, as well as improved dewatering rates and fine-particle retention — often when using lower qualities of fiber furnish or reduced basis weights — there is a continuing need to consider different combinations of chemical additives. Attention to the charged character of additives, supplemented by measurements of cationic demand and zeta potential, can be tools in optimizing such additive programs.

The premise of this paper is that charged water-soluble additives in the papermaking process do not act alone. Rather, their effects can depend on the presence and levels of other substances in the mixture. This paper focuses on carboxymethyl starch (CMS), the most prominent function of which can be to increase the bonding strength among fibers during the produ+ction of paper. The chemical synthesis of CMS and related chemicals, as well as its properties, have been discussed by Heinze and Koschella [1].

There are several motivating reasons to consider CMS as a papermaking additive. To begin, it is based on a photosynthetically renewable product, starch. In addition, unlike many strength-enhancing additives for paper machine wet-end addition, CMS has a negative ionic charge. When one considers the generally negative charge of most untreated papermaking fibers, as delivered from the pulp mill, the negative (anionic) charge of CMS can raise some interesting issues. However, sometimes an anionic additive can be used to balance the charge demand in the process water. As has been noted by others, papermaking outcomes including drainage rates, efficiency of retaining fine particles, and the effectiveness of strength agents and sizing agents is often maximized when the colloidal charges in the wet end are approximately balanced [2-6].

One way to take advantage of anionic polymers as strength additives in papermaking can be called the "anchoring point" strategy. This entails first treating the fiber furnish with a positively charged additive, such as a cationic polymer or a soluble aluminum-based product, e.g., papermaker's alum (aluminum sulfate). The cationic additive will tend to adsorb onto the fiber surfaces, creating positive sites that then can bind to negatively charged substances added later. For example, one of the earliest synthetic dry strength agents was a copolymer of acrylic acid and acrylamide [7-8]. This additive was retained by first treating the fiber slurry with alum. Under the weakly acidic conditions employed, the alum provided the positively charged sites on the fiber surfaces, allowing for the anionic acrylamide copolymer to be well retained. In related work, Song and Hubbe [9] enhanced paper strength by sequential addition of alum, followed by carboxymethylated beta-*D*-glucan obtained from oat spelts. Additional work by the same authors demonstrated similar results when using alum followed by anionic beta-*D*-glucan that had been prepared by TEMPO-mediated oxidation [10]. Watanabe et al. [11] achieved similar results with carboxymethylcellulose (CMC), except that they used an opposite order of addition. In related work [12], the first additive (cationic) was poly(diallyldimethylammonium chloride) (polyDADMAC), and this was followed by CMC. The highest gains in paper strength were achieved when the amount of the cationic polymer was added at its saturation level; in other words, no more of the cationic additive was able to adsorb onto the cellulosic fibers. Aarne et al. [13] carried out further experiments to clarify the mechanisms by which cationic polyelectrolytes can affect the adsorption of CMC onto fiber surfaces.

An alternative mechanism by which an anionic dry strength polymer can be induced to precipitate and deposit onto cellulosic fiber surfaces involves the formation of polyelectrolyte complexes (PECs) [14-15]. Some of the earliest reports of paper strength improvements as a result of PECs were published by Carr et al. [16-17]. They showed that paper strength could be increased when the fiber furnish was treated sequentially with starch xanthate (anionic) and a cationic resin. More recently, this approach has been demonstrated with sequential addition of polyDADMAC and CMC [18-19]. The effectiveness of the bonding system was also demonstrated in the case of non-bonding glass fibrids, which were formed into stiff, paper-like sheets [20]. Related work has been reported by Gärdlund et al. [21] and Fatehi et al. [22]. While the observed strength improvements when using PECs were high in comparison to conventional dry strength additives for paper, two matters of concern should be considered. The first is the relatively high costs associated with treatments that involve more than one charged additive. The second is a tendency for PECs to deposit onto papermaking equipment, including forming screens. Work by Heerman et al. [23] showed that undesirable deposits could be minimized when the oppositely charged polymers were added sequentially to the fiber suspension with effective agitation. That method was called in-situ formation of PECs.

A third approach, which has achieved outstanding results in the laboratory, is called layer-by-layer assembly of polyelectrolyte multilayers. As the term implies, the surfaces are exposed successively to solutions of oppositely charged polyelectrolytes, often with rinsing steps and optional drying steps interposed [24]. Wågberg et al. [25] were among the first to apply this approach to the treatment of papermaking fibers, thereby achieving a strong increase in interfiber bonding. The main drawbacks of the layer-by-layer technology are the need for relatively large numbers of sequential treatments and the fact that process water available within typical paper machine systems will already contain an assortment of charged components.

Though carboxymethylated polysaccharide products are not usually regarded as additives for hygiene tissue products, their usage makes logical sense as a way to enhance the overall effect of certain net cationic strength additives, such as glyoxylated polyacrylamide (gPAM) products. It has been shown that the effects of wet strength additives are sometimes enhanced by subsequent addition of an anionic polymer (such as CMC, or carboxymethylated glucomannan) to the furnish [26-27]. In addition to helping achieve a favorable charge balance, the beneficial results also could be attributed to covalent reaction between the CMC and the permanent wet strength agent utilized in the work just cited. This concept was supported by follow-up work [28]. In a related study, high wet strength was achieved when using the opposite order of addition, wherein calcium chloride was used to fix the CMC onto fibers before the addition of the wet-strength agent [29].

The goal of the present work was to study factors affecting the use of CMS as a dry strength agent under alkaline papermaking conditions. Thus, unlike some of the studies cited previously [7-11], it would not make sense to employ alum as a cationic agent, since alum loses its positive charge at neutral or higher pH. Cationic additives considered in this work, for use in sequential combination with CMS addition, include gPAM products, poly(vinylamine) (PVAm), and an acrylamide-based cationic retention aid. As a working hypothesis, it was assumed that results would be affected by the balance of colloidal charges in the fiber suspension.

EXPERIMENTAL

Chemicals and materials

The chemical additives and pulp suspension used in the present work were essentially the same as those in a companion study by Putney et al. [30], which focused on the effects of tissue paper additives on the paper production issues and product quality of paper made from recycled copy paper furnish. As reported in the cited work, the filler content of the copy paper was determined to be 22.7% (air-dry), based on an assumption that 100% of the mineral content had been calcium carbonate. The main additives related to the content of this article are listed in **Table I**.

The Hercobond and Sokalan products were liquid concentrates, which were made down to aqueous solutions of 1% solids before usage. The Aquagel product was a dry

Brand name	Description
Hercobond 1315	Glyoxylated polyacrylamide (PAM) temporary wet strength resin, Solenis (Wilmington, DE, USA; gPAM2)
Hercobond 1307	Glyoxylated PAM temporary wet strength resin, Solenis (gPAM1)
Hercobond 6350	Polyvinylamine dry strength technology, Solenis (PVAm)
Aquagel 220 UL	Carboxymethyl starch (CMS), anionic strength agent, Aquasol (North Tonawanda, NY, USA)
Sokalan PA 40	Dispersant: Sodium polyacrylate, BASF (Ludwigshafen, Germany)

I. Principal chemical additives associated with this work.

powder that was dissolved in water with stirring for 1 h to prepare a 1% stock solution. In this paper, addition levels are expressed as a percentage of active material (dry basis) to dry furnish solids.

Laboratory tests

Procedures employed for the evaluation of retention, dewatering rates, and flocculation were the same as those used in the companion study by Putney et al. [30]. Likewise, the same methods were employed for evaluation of zeta potential values (from fiber-pad streaming potential tests) and charge demand (by polyelectrolyte titration to a zero endpoint with a streaming current detector).

Handsheet preparation

Paper handsheets were prepared as described by Putney et al. [30], with a key exception. It had been observed in the course of carrying out other tests that combinations of CMS and various cationic additives often produced noticeable levels of flocculation in the fiber suspensions. As a means to compensate for that tendency, a kitchen blender was employed during the preparation of handsheets. Specifically, a Hamilton Beach "Blend Master" was run for 10 s at its lowest ("Whip") setting after each successive chemical addition, still at a 0.5% solids consistency. After the final chemical addition, the blended furnish was added to the mold of the handsheet apparatus, whereafter the procedures for TAPPI Standard Test Method T 205 "Forming handsheets for physical tests of pulp" were followed.

Tensile testing

All handsheet tensile properties were measured with a Messmer Büchel horizontal tensile tester (Lorentzen & Wettre; Kista, Sweden) following guidelines from TAPPI T 494 "Tensile properties of paper and paperboard (using constant rate of elongation apparatus)" and T 220 "Physical testing of pulp handsheets." After visually checking, to avoid regions with nonuniformity, a 15-mm-wide strip of paper was cut from the center of the handsheet and set into the jaws of the tensile tester. These were initially spaced 100 mm apart, but moved farther from one another as the test proceeded. Strength data were collected until structural failure (breakage of the paper strip).

Air permeability

A manual Gurley densometer was used to determine the air permeability of the handsheets as instructed by TAPPI T 460 "Air resistance of paper (Gurley method)." The top cylinder of the densometer was raised until catching onto a ledge, such that 100 cc of air was entrained inside the inner chamber. A handsheet sample was secured into the lower clamp, and then the cylinder catch was released. The time required for 100 cm^3 of air to flow through the handsheet was recorded by the device.

RESULTS

Zeta potentials

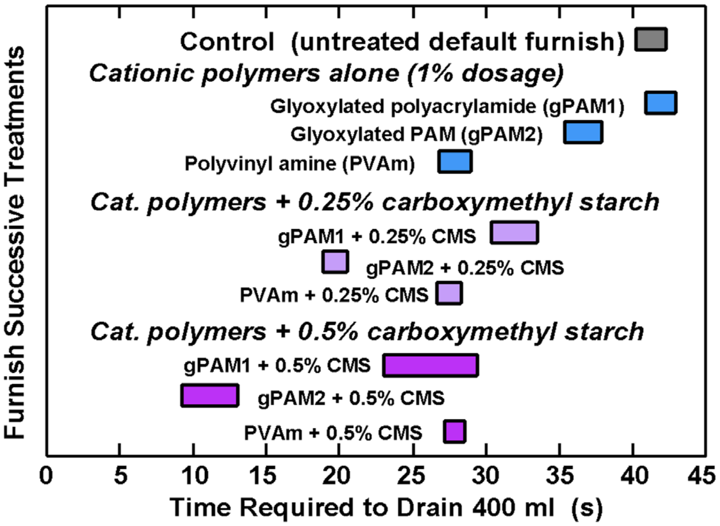
Calculated zeta potential values, derived from the fiber-pad streaming potential tests, exhibited consistently negative values for the range of conditions considered in this work. In particular, the control (untreated furnish) exhibited fairly consistent zeta potentials in the range of -20 to -25 mV, based on tests from multiple groups of experimenters. Polyacrylate dispersant, which has a strong negative charge, had little to no effect on the zeta potential at any concentration when added alone to the default furnish. This is consistent with an expected lack of adsorption of an anionic polymer onto a negatively charged untreated fiber surface. Somewhat different results were obtained for CMS. Low-concentration additions (0.1% based on solids) of CMS to the control stock had no statistically significant effect on zeta potential; however, at higher concentrations, the zeta potential grew less negative (decreased in absolute magnitude). Thus, CMS dosages at a level of 1% by fiber mass shifted the zeta potentials to a broad range of -22 to -5 mV. These results suggest, firstly, that CMS adsorbed onto the fiber surfaces, and secondly that the presence of adsorbed CMS may have pushed the hydrodynamic slip plane farther out from the cellulosic surfaces, thus giving less negative zeta potential values.

Further details regarding the zeta potential measurements of treated recycled copy paper furnish can be found in a companion study to this paper [30]. The scope of this previously reported data extends beyond CMS and into a variety of common tissue papermaking additives.

Charge demand properties

The influence of CMS on charge demand was tested under two conditions: as the only additive in the recycled copy paper furnish, and following the addition of a PVAm dry strength aid. To account for the pH-dependency of the cationic properties of PVAm, these measurements were taken at varying pH levels. Some lab teams recorded the pH values unaltered, while others were instructed to manipulate the pH by adding sodium hydroxide (NaOH) to the furnish.

Compared to control stock samples, the presence of CMS alone generally increased the cationic demand across all pH levels. This was expected, as the addition of an anionic polymer into a solution should logically contribute to its negative charge. However, at a 0.2% addition based on fiber mass, these jumps in cationic demand were not large enough to be considered statistically significant. When CMS (at a 0.2% dosage level) was combined with PVAm (at a 0.5% dosage level), the cationic demand tended to decrease. The majority of these changes were also deemed statistically insignificant, except at pH values around 10.5 or higher. Whereas the control and CMS-only samples experienced heightened cationic demand at higher pH, the samples with both CMS and PVAm had charge demands that remained steady regardless of pH value.



1. Effect of CMS on drainage rate at different dosage levels, when added to the furnish after one of three cationic strength aids (all at a 1% dosage based on solids).

In summary, though CMS alone or in combination with cationic additives had detectable effects on charge demand, such effects were not large relative to corresponding measurements of the default furnish. Further details and results related to the charge demand effects of other additives were reported in another paper [30].

Dewatering rate

All samples in the dewatering tests (excluding the control furnish) had a 1% dosage of cationic strength aid solids by fiber mass. The impact of subsequent addition of CMS on dewatering rate was made apparent by varying the dosage of CMS in each furnish treatment. As shown in **Fig. 1**, the addition of cationic strength aids (by themselves) moderately reduced drainage times, with the exception of the medium-charge glyoxylated polyacrylamide (gPAM1). The high-charge glyoxylated polyacrylamide (gPAM2) and PVAm decreased drainage times, presumably boosting the retention of fine materials and opening up drainage channels in the fiber network.

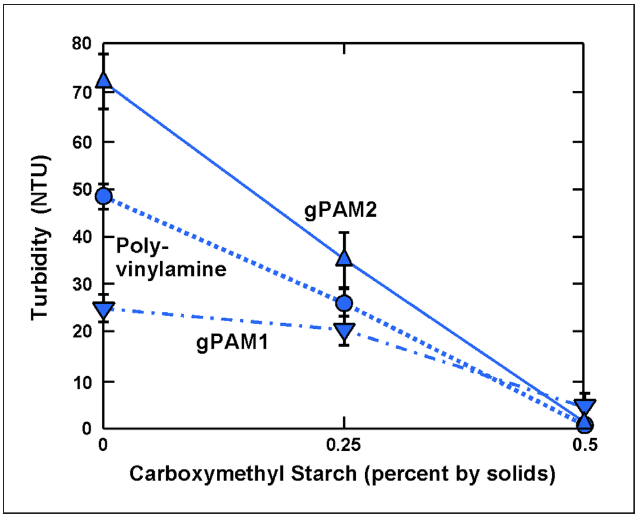
As shown by the middle and lower groups of results in Fig. 1, subsequent addition of CMS after the cationic additives did not have a consistent effect on drainage rate across all kinds of cationic strength aids. When CMS was introduced to samples treated with either type of gPAM (both cationic), the drainage rate increased dramatically. Although variation increased with the CMS amount, drainage times were statistically lower at dosage levels of both 0.25% and 0.5% of the fiber mass. Remarkably, samples including the larger dosage of CMS and stronger charge of gPAM reduced the drainage time from roughly 40 s (untreated) to a little more than 10 s. The presence of CMS in systems with PVAm, conversely, had no effect on drainage rate. This was recognized at both dosage levels of CMS, with variation improving minimally.

Of the three strength additives, when used alone, the most promising effects related to dewatering were obtained with the PVAm. However, subsequent additions of CMS, at either of the two levels, had no significant effect on dewatering. Increases in filtrate mass were not found to be statistically significant, and variation increased tremendously with the amount of CMS present. More research will be needed to examine how PVAm influences the dewatering rate, especially when accompanied by other additives in the papermaking system.

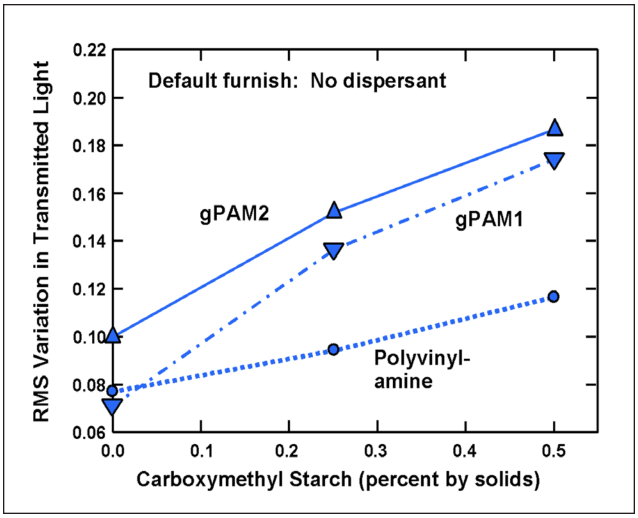
Retention efficiency

The same experimental conditions utilized during dewatering tests were repeated in Britt jar tests to evaluate effects on fine particle retention. The turbidity of filtrate from samples with different cationic strength aids (gPAMs and PVAm) was detected before and after the addition of CMS to the system. **Figure 2** shows that the addition of CMS kept fine material attached to fiber surfaces, thus increasing their retention in the sheet. At a dosage level of 0.5% of the fiber mass, the filtrate turbidity was decreased well below 10 NTU for all cationic strength aids. Even at a dosage of 0.25%, the reduction in filtrate turbidity was statistically significant for samples including gPAM2 or PVAm. As shown in Fig. 2, two of the cationic additives, in combination with increasing amounts of CMC, gave a nearly linear effect on filtrate turbidity.

The same series of tests was repeated in furnish that had been pretreated with a 0.1% addition of polyacrylate dispersant. The results are listed in **Table II**. As shown, the same trends generally redeveloped, albeit not as pro-



2. Effect of CMS on filtrate turbidity with pretreatment by different cationic strength aids at the 1% level based on solids.

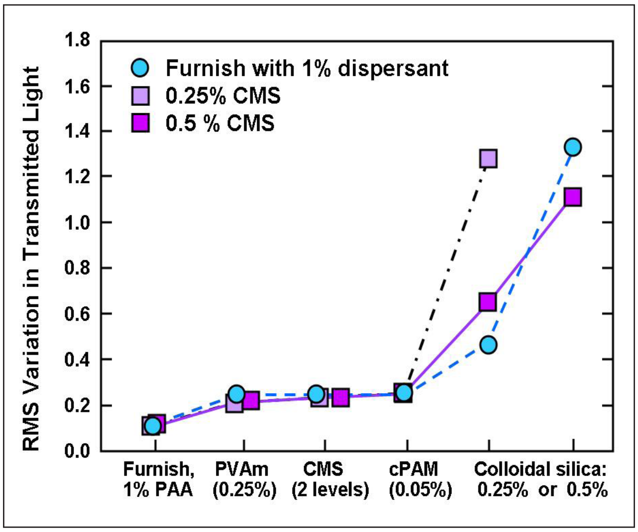


3. Effect of CMS on root mean square (RMS) variation in transmitted light for dispersant-free furnishes.

nounced as before. The CMS added to the furnish that had been treated with high-charge cationic polymers led to increased overall retention efficiency. In furnishes with low- to medium-charge cationic polymers, the effect of CMS addition was less predictable. Interestingly, the control stock sample saw massive improvement in retention with the presence of CMS despite there being no cationic strength agent present. Perhaps this indicates that the recycled copy paper furnish already had moderate concentrations of positively charged substances present before experimentation began, thus providing anchoring points for the CMS.

Fiber flocculation

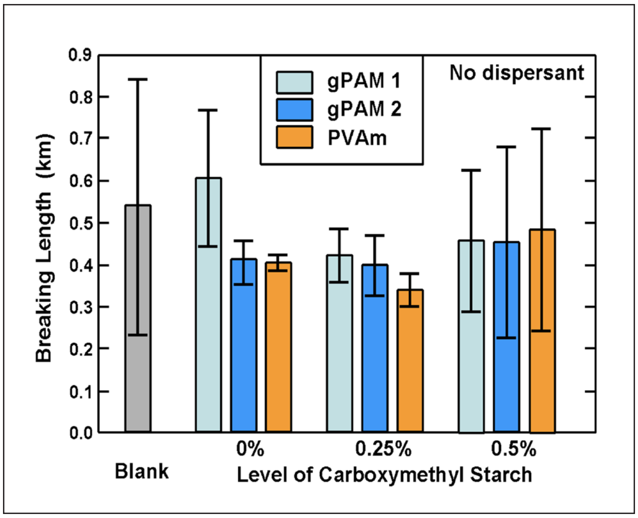
When introduced to the default furnish, the combinations of a cationic strength aid followed by CMS resulted in a minor jump in flocculation. **Figure 3** displays how the root mean square (RMS) variation in transmitted light was affected; at CMS dosage levels of 0.25% by fiber mass, the RMS variation increased by no more than 0.06, regardless of what strength aid was present. Subsequent increase in the CMS concentration had an even smaller change on RMS variation. In particular, samples with PVAm showed little impact on flocculation due to CMS. Though it was statistically significant (due to near-absent variability), the RMS



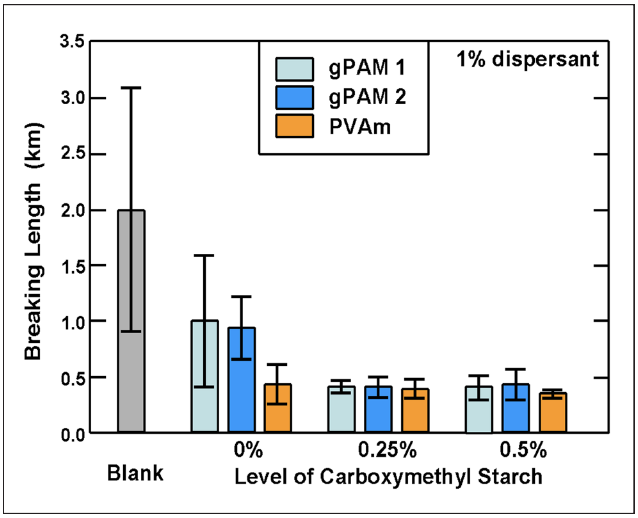
4. Effect of CMS on fiber flocculation following subsequent additions of cPAM and colloidal silica. Sequential treatments were as follows: default furnish pretreated by 1% dispersant; then PVAm at the 0.25% level; then either zero or 0.25% or 0.5% CMS (see symbol colors); then cPAM at the 0.05% level; and finally colloidal silica at the cumulative dosages of 0.25% and 0.5%.

Cationic Additive	Cationic Additive Alone at the 0.5% Solids Level	Cationic Additive (0.5%) Followed by 0.5% CMS
gPAM1	95.9	15.9
gPAM2	29.4	30.4
PVAm	26.5	12.2
Control (no cationic additive)	100.1	43.7

II. Filtrate turbidity (NTU) from furnish that had been pretreated with 1% polyacrylate dispersant, then optional addition of a cationic polymer (0.5% level), and finally carboxymethyl starch (CMS) at the 0.5% level



5. Effect of CMS on the breaking length of dispersant-free samples with differing cationic polymers.



6. Effect of CMS on the breaking length of dispersant-dosed samples with differing cationic polymers (at the 0.5% addition level).

variation increased by less than 0.03 at a CMS addition of 0.5%.

However, when the combination of CMS and a cationic strength aid was followed by successive additions of cationic retention aid (such as cPAM) and colloidal silica, fiber flocculation levels substantially increased. This phenomenon is illustrated in **Fig. 4**. Additions of CMS (at both the 0.25% and 0.5% dosages) did not significantly change the flocculation behavior resulting from the polyacrylate dispersant and PVAm. Rather, the RMS variation remained constant until colloidal silica was added. At the 0.25% addition of colloidal silica, the CMS actually served as the better flocculating agent, tripling or quadrupling the RMS variation in transmitted light. The final data point for the 0.25% CMS level is missing from the figure due to severe flocculation in the suspension, which clogged the peristaltic pump used for those measurements.

The results just shown suggest the possibility of forming polyelectrolyte complexes (PECs) as a means of intentionally creating flocculation.

Handsheet properties

To analyze the effect of CMS on resulting paper porosity and tensile strength, two sets of handsheets were created. In the first, a cationic strength aid (one of the gPAMs or PVAm) was introduced at a 0.5% dosage (by fiber mass) into the untreated furnish. This was followed by the addition of CMS into the system at one of three levels: 0%, 0.25%, or 0.5%. The second set of handsheets was prepared identically to the first, except that 1% of polyacrylate dispersant was included in the stock furnish. This modification drastically enhanced the strength of the control and 0% CMS samples — an effect that can be attributed to lowered filler retention (due to the anionic properties of the dispersant). In addition, it is speculated that another contribution to higher sheet strength was a more uniform sheet structure, i.e., better formation in the presence of the dispersant.

As shown in **Fig. 5**, the handsheets prepared from the default furnish (without additives) exhibited among the highest tensile strengths. This goes against prior research that had suggested that the deposition of polyelectrolyte complexes (like those formed during this experiment) boosted paper strength. The reason for this discrepancy is unknown, but the data obtained here shows no statistically significant increases in tensile strength associated with cationic polymers or CMS. In fact, the presence of cationic polymers typically reduced tensile strength, and the subsequent addition of CMS (at either dosage) caused no significant changes. As noted previously, lower strength measurements relative to the control sheets might be due to higher filler contents and degrees of flocculation in the presence of the cationic strength aids and CMS. Additional research will be necessary to explain these results.

As shown in **Fig. 6**, remarkably higher (but variable) strength values were observed when the default furnish had been pretreated with a relatively high level of anionic dispersant (1%). The vertical scale of Fig. 6 had to be changed relative to Fig. 5 in order to show those values. Note also that the remaining histogram bars in Fig. 6 represent strength levels either above or in a similar range to those shown in Fig. 5.

Large relative decreases in the paper's tensile strength were observed upon addition of the cationic strength agents to stock that had been pretreated with anionic dispersant at the 1% level based on solids. Further addition of CMS at either the 0.25% or 0.5% level decreased the strength or had no effect, in different cases. The lowest strength results shown in Fig. 6 were in a similar range as those shown in Fig. 5 for dispersant-free systems. One hypothesis that might account for such effects for the dispersant-containing system is that a polyelectrolyte complex-

Cationic Additive	Pretreatment with Dispersant at 1% Solids Level	Cationic Additive Alone at the 0.5% Solids Level	Cationic Additive (0.5%) Followed by 0.5% CMS
gPAM1	No	6.8 (0.66)	7.9 (0.37)
gPAM2	No	4.9 (1.44)	5.8 (0.42)
PVAm	No	6.4 (1.84)	6.7 (2.83)
(no cationic additive)	No	6.0 (0.79)	-
gPAM1	Yes	7.3 (2.11)	11.3 (1.50)
gPAM2	Yes	11.1 (2.28)	12.5 (0.68)
PVAm	Yes	14.1 (1.02)	14.0 (0.95)
(no cationic additive)	Yes	18.7 (11.85)	-

III. Gurley densometer porosity (seconds per 100 cm^3) of handsheets optionally pretreated with polyacrylate dispersant, followed by additions of cationic additives and CMS.

ation between the dispersant and the cationic strength polymers led to fiber flocculation, thus decreasing the paper's uniformity. Such an effect would be expected to make the resulting paper more porous, which provides a way to test the hypothesis.

Porosity results are shown in **Table III** from the same handsheets tested in Fig. 5 and Fig. 6. Contrary to the hypothesis just proposed, the handsheets prepared after pretreating the furnish with dispersant generally showed lower porosity (i.e., higher amounts of time required for passage of 100 cm^3 of air). Though the addition of gPAM and PVAm to the dispersant treated furnish decreased the time for air permeation, the values remained higher than for corresponding tests in the absence of dispersant. The fact that the sheets pretreated with dispersant were more resistant to air permeation is inconsistent with the proposed strong flocculation of the fibers. Rather, as would be expected from the name "dispersant," it appears that those sheets were sufficiently uniform to effectively block the passage of air.

The idea that greater uniformity was associated with the action of the dispersant is supported by data in the last row of Table III. This row corresponds to a default condition in which the 1% dispersant addition was the only treatment. The fact that the Gurley seconds result for that condition (18.7 s) was so much higher than for the corresponding tests in the absence of dispersant (6.0 s) suggests that the dispersant had a large effect in dispersing the fibers and facilitating preparation of a dense, uniform sheet.

DISCUSSION

There appear to be two main lessons provided by the results of the experiments described in this study. The first is that interactions among different ionically charged additives to a papermaking process can have dominant effects. The other appears to be that, when using types of additives not often implemented in paper mills, those effects will not necessarily be favorable to all of the measured paper properties or factors affecting the papermaking process.

Effects of charge were apparent in the drainage results. As was shown in Fig. 1, changing the ratios between the dosages of charged additives had very large effects on the time required to drain specified volumes of filtrate. Likewise, fine-particle retention results also appeared to be closely associated with the proportions of oppositely charged additives.

In addition to charge, it appears important to focus on characteristics of polyelectrolyte complexes formed among two or more water-soluble polymeric additives in the mixture [14-15]. Combinations of cationic strength additives (especially gPAMs) and CMS were found to increase levels of fiber flocculation. However, much larger and more intense flocculation was observed upon further addition of negatively charged colloidal silica nanoparticles to the mixture. There is reason to suspect that the detailed structures and behavior of polyelectrolyte complexes will depend on quasi-irreversible processes, which might be influenced by details of the orders of addition [31]. Future research might follow up by focusing on the sizes and other aspects of polyelectrolyte complexes, either in the absence or the presence of papermaking fibers.

Demonstrating strength improvements of laboratory-formed paper specimens, by use of polymeric additives, can be a challenging task. Unlike a commercial papermaking operation, most handsheets are made such that filtrate is discarded after each sheet. As a consequence of variations in retention efficiency, the contents of various fine particles within handsheet specimens may be lower than what would be expected under steady-state conditions in which most of the process water is reused multiple times. Because any unretained filler particles, cellulosic fines, and other small particles build up in the process water of a paper machine, the sheet's composition tends to be less sensitive to differences in retention efficiency. An added complication is that the strength properties of paper tend to be hurt by increasing levels of mineral fillers [32-33] and inducing non-uniformity by action of polymers or their combinations [34]. For all of these reasons, the strength results shown in Fig. 5 (in the absence of dispersant) have to be regarded as inconclusive. It is quite likely that conditions during full-scale papermaking would have different overall effects on such things as the uniformity of the paper, which would affect operational outcomes, as well as strength. In addition, relatively high levels of additives had been selected for this study, for the purpose of finding statistically significant effects.

The idea that higher filler content could be responsible, in part, for the lower tensile strength of handsheets that had been prepared with some combinations of gPAM and CMS is consistent with the retention results shown earlier in Table II. In addition, a future study in this same series of work will report some results of tests in which the filler content of handsheets had been evaluated. That same article also will include evaluation of handsheet uniformity. However, based on the present results, one can expect that optimization of the type of additive program explored in the present work will require careful testing of various options. Variables to consider when implementing such an additive program on a commercial paper machine could include the time gap between sequential addition points, details of mixing at points of injection, whether or not the cationic additive is being used to provide anchoring points for an anionic additive, and whether or not to pre-mix oppositely charge additives.

The remarkably high strength that was achieved when the default furnish was treated with anionic dispersant at the 1% level seems to fall outside of the scope of conventional papermaking. The fact that the polyacrylate dispersant used in the present work had a high anionic charge but a relatively low molecular mass (15,000 g/mole) means that it is unlikely to function in the manner of a conventional formation aid. Formation aids, which consist of very high-mass water-soluble polymers, are widely used in both traditional and handmade papermaking [35-36] and in making wet-laid nonwoven sheets from long fibers [37-39]. In such cases, the high viscosity of the polymer additives can remarkably slow down the rate of dewatering, which was not observed in the present work when the dispersant was present. It makes sense that an additive that tends to disperse suspended particles will favor excellent uniformity of the resulting paper sheets and low levels of retained mineral particles — both tending to favor high strength. Due to the large strength improvements seen in the present work, both with the dispersant alone and in combination with the gPAM polymers at the 0.5% level, it would make sense to carry out additional testing — especially in the absence of mineral fillers.

CONCLUSIONS

Laboratory experiments involving recycled copy paper furnish showed that various effects of CMS were highly dependent on its interactions with other charged materials in the suspension. Addition of cationic polymers, followed by CMS, gave rise to substantial increases in dewatering rates and fine particle retention. Furthermore, fiber flocculation was increased when the furnish first was treated with cationic gPAM strength agents before the CMS. Such effects were found to be sensitive to the levels of the oppositely charged additives. Effects of CMS on strength properties were mixed, which might have been due to unavoidable differences in filler contents or uniformity levels of sheets formed after different chemical treatments. Unexpectedly high paper strength was observed for paper made from the default copy paper that had been treated with an anionic dispersant alone. Subsequent addition of CMS did not contribute to the strength of such handsheets, with or without the addition of cationic polymers after the dispersant. **TJ**

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ABOUT THE AUTHORS

Carboxymethylated starch (CMS) has potential usage to promote bonding of paper, but it also requires interactions with cationic additives and can affect retention, drainage, and formation. This study is part of a series in which researchers Putney et al. at North Carolina State University evaluated effects of tissue additives, which also appears in this current issue of *TAPPI Journal* on p. 67.

In this study of CMS, the effects of charge, flocculation, and retention of filler required that multiple different tests were carried out. Overall, the researchers did not expect such a significant effect from the addition of a dispersant.

This study will be of interest to mills, as there has been a relative lack of information about combinations of different additives and how they affect papermaking. The present work revealed a need for follow-up work concerning poly(vinylamine) (PVAm), which will be available in the near future.

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