

Dry-Strength Development by Polyelectrolyte Complex Deposition onto Non-Bonding Glass Fibers

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Sheets formed from glass microfibers had almost zero tensile strength in the absence of polymer treatment, but paper-like dry-strength was achieved if fiber suspensions were treated with combinations of a cationic and an anionic polyelectrolyte before sheet formation. Strength increases generally were maximized when the ratio between the cationic poly-(diallyldimethylammonium chloride) and carboxymethylcellulose was within about 2:3 and 3:2 stoichiometry of charged groups on the macromolecules. Sequential addition of the polyelectrolytes to fiber slurry generally yielded higher strength than pre-mixing the polyelectrolytes before their addition. Significant effects were observed, depending on the ratio of the two polyelectrolytes, optional cationic pretreatment of the fibers, salt concentrations, and the elapsed time between mixing of polyelectrolytes and their addition to a fiber slurry. Time-dependent electrostatic interactions appear to control the deposition of polyelectrolyte complexes, and it was found that the details of chemical addition strategies can have major effects on the results.

INTRODUCTION

Papermaking additive strategies involving sequential addition of positive and negative polymeric colloidal materials or polyelectrolytes have been known at least as early as 1940 [1]. Reported benefits have included improved first-pass retention and dewatering rates [2-3], and enhancement of the paper's dry-strength [4-13].

Polyelectrolyte complexes also have been studied as a means of modifying the surface properties and colloidal stability of various dispersed systems [14-16]. More recently, evidence has been presented that deposition of polyelectrolyte complexes onto cellulosic substrates takes place during ordinary papermaking practices [17].

Interest in high-performance dry-strength additive systems is motivated by several factors, including the reduced bonding strength of recycled fibers [18] and efforts to achieve higher strength-to-weight ratios in paper products. Papermakers often can achieve their base-sheet strength objectives through conventional approaches, including increased refining [19], and by use of wet-end chemical additives, such as cationic starch [20-21]. However, each of these approaches has practical limits. Excessive refining tends to increase apparent density and increase the brittle nature of paper [19]. Strategies involving the addition of a single polyelectrolyte, such as cationic starch, tend to be limited by the ability of various types of fiber surfaces to accommodate no more than about 1-1.5% of such additives, on a mass basis.

Recently several studies have reported superior gains in dry-strength when a pair of oppositely charged polyelectrolytes was added sequentially to papermaking furnish. For example, it has been found that sequential addition of anionic starch and a cationic polymer was able to retain over 5% of starch added at the wet end of a paper machine,

achieving strength increases similar to those often associated with size-press addition of starch [22-23]. Other work has shown substantial strength gains by interacting cationic wet-end polymers with anionic colloidal substances already present in the furnish [24]. Subsequent work showed that pre-formed complexes between lignin byproducts and cationic starch resulted in higher dry strength gains, compared to treatment by the cationic starch alone [25]. In other work it was shown that substantial increases in strength can be achieved by pre-mixing of solutions of a positively charged polyamide resin and negatively charged carboxymethylcellulose (CMC) before their addition to papermaking fibers [12,25]. Previous work in this laboratory showed that the effectiveness of a dual-polymer dry-strength system could be maximized in certain cases if the dosage of the first, cationic additive was matched to the adsorption capacity of the fiber surfaces [7]. Finally, an innovative study by Wågberg *et al.* [26] showed that successive deposition of as many as 20 layers of positive and negative polyelectrolytes on cellulosic fibers yielded progressive increases in the dry strength of the resulting paper. Foundational studies of polyelectrolyte multilayers have been reviewed by Decher [27].

A motivation for the present study was to understand the charge relationships governing the efficiency of polyelectrolyte adsorption onto fiber surfaces in cases where the adsorbed amount of either polymer alone greatly exceeds the adsorption capacity of the fibers, under the electrolyte conditions employed. A preceding study involving adsorption of polyelectrolyte complexes onto recycled bleached kraft fibers [10] involved measurements of turbidity. Results showed that pre-formed complexes, containing different ratios of poly-(diallyldimethylammonium chloride) (poly-DADMAC) and carboxymethylcellulose (CMC) were retained at high amounts on the fibers over a wide

range of conditions, with a weaker than expected dependence on the measured zeta potentials of the suspended materials. In particular, pretreatment of the fibers with sufficient poly-DADMAC to saturate the adsorption capacity of the surfaces had a beneficial effect on retention of the polyelectrolyte complexes, regardless of their net charge. These results were in contrast to those reported by Kekkonen *et al.*, who studied deposition of polyelectrolyte complexes onto silica wafers [28]. It was thought that a possible explanation for the different results might involve the expected higher charge density of the silica, compared to the recycled fibers.

Another line of questions that was not settled by the previous work was whether or not the electrokinetic properties of the substrates and of the polyelectrolyte complexes were, by themselves, able to account for the efficiency of polyelectrolyte retention on solid substrates under varying electrolyte conditions, charge ratios, and orders of addition. Previous work in our lab had shown that the order of addition of polyelectrolytes can make a substantial difference in charge-related phenomena [29-30]. Because of time-dependent processes, as polyelectrolytes gradually adopt more thermodynamically favorable conformations within complexes [31-32], it is reasonable to expect the presence of uneven charge distributions on the outer areas of the complexes. This will be true especially at the limit of high molecular masses and short equilibration times. Non-equilibrium factors also might be expected to cause deviations from simple relationships between measured zeta potentials of polyelectrolyte complexes, relative to their tendencies to adsorb onto either positive or negatively charged substrates. Related time-dependent effects, providing evidence of gradual conformational changes, have been noted for polymer-fiber interactions [33-34].

Glass microfibers were selected as the substrate of choice for the present work for a number of reasons, including the opportunity to settle issues just noted related to polyelectrolyte interactions with a silicon-based substrate. The glass microfibers can be considered as a simplified model of cellulosic fibers, avoiding complexities related to porosity, swellability, and the presence of a substantial level of fines. The charge characteristics have some resemblance to those of cellulosic fibers, since both tend to develop a more negative zeta potential with increasing pH, due to dissociation of weak acidic groups [35-37]. Preliminary tests indicated that the glass microfibers were easily dispersible in aqueous solution and it was possible to form handsheets in the usual way. Sheets formed in the absence of polyelectrolytes had almost zero tensile strength, making it possible to attribute essentially all of measured strength to the effects of additives. Finally, the ability of the glass fibers to withstand incinerating temperatures of 450 °C without significant loss of mass opens the opportunity to use a gravimetric approach to determine the uptake of combustible polyelectrolytes on the fiber surfaces.

EXPERIMENTAL

Materials

Solutions and suspensions were prepared with deionized water having an initial conductivity less than 2 $\mu\text{S}/\text{cm}$. All chemical additives were of reagent grade. The background electrolyte used for most of the experiments was prepared with 10^{-4} M sodium bicarbonate and sufficient sodium sulfate to achieve an electrical conductivity of 1000 $\mu\text{S}/\text{cm}$ at the laboratory temperature of approximately 23 °C. Experiments involving different concentrations of Na_2SO_4 are noted in the text. The pH was buffered

at a value of 7.0, except in noted cases where adjustments were achieved with either NaOH or H₂SO₄.

The poly-base used in the research, obtained from Fisher (Cat. No. 40,903-0) was “high mass” poly-(diallyldimethylammonium chloride) (poly-DADMAC), having a stated mass of 400,000 to 500,000 Daltons. Certain supplementary tests, identified later by the term “low mass” poly-DADMAC involved a Fisher product (Cat. No. 40,901-4), having a mass of 100,000 to 200,000 Daltons. Solutions having 1% polymer by mass were prepared with deionized water.

The poly-acid used in the work was carboxymethylcellulose CMC 7M, obtained from Hercules, Inc. This product has an average of about 0.7 carboxymethyl groups for each anhydroglucose unit. Solutions of 1% solids were prepared by gentle overnight stirring with deionized water.

The glass fibers were of type C-50-R, obtained from Lauscha Fiber International. These fibers, prepared by rotary attenuation, have an acid-resistant borosilicate glass composition. The average fiber diameter is 4 μm and the average length is about 4 mm. For certain of the work to be described, involving streaming potential measurements (*e.g.* Fig. 1), the average fiber length was decreased by passing the fibers four times through a paper shredder (Novitech Model PS 026/B1), having a 4mm distance between adjacent cutting elements. The device was modified with a “hopper” to accommodate approximately 50 ml of dry fiber at one time, and the fibers were fed safely into the cutting zone with a specially designed plastic tool. Before use, the cutting elements were extensively rinsed with acetone to remove any oils. Unmodified fibers were used for all other experiments, not having to do with streaming potential analysis.

Streaming Potential Analysis of Glass Fibers

Streaming potential measurements, as a function of pH or poly-DADMAC addition, were obtained by dispersing 4.0 g of glass fibers into 800 ml of default buffer solution. The fiber length had been reduced, as described earlier (see Materials). The analysis was carried out with the Streaming Potential Jar (SPJ) device described elsewhere [38]. Briefly stated, the slurry was continuously stirred within a sealed pressure jar. A “high” pressure of 207 kPa (30 psi.) was used to force the slurry towards a submerged screen, causing a pad of fibers to form on the screen. Filtrate passed through the screen, out of the jar through a sealed tube, and into a beaker on an electronic balance, where it was continuously weighed. Meanwhile, the potential difference between metal probes on each side of the screen was continuously monitored. At the end of 10 s of “high” pressure, the pressure was suddenly decreased to ambient, and reference potential data were obtained, making it possible to calculate the streaming potential, by difference. Other parameters monitored during each cycle of testing were filtrate turbidity, electrical conductivity, and pH. At the end of each cycle, vacuum was automatically applied to draw all of the filtrate back into the jar, so that the apparatus was ready for a subsequent cycle. To adjust the pH, when this was necessary, either sulfuric acid or sodium hydroxide solution was injected into the returning flow at the start of the vacuum application. Likewise, known amounts of dilute poly-DADMAC solution also could be injected into the return flow during successive cycles of operation of the device, making it possible to carry out titrations. The contents of the jar were subjected to an additional 10 s of magnetic stirring before the start of each high-pressure application.

Streaming Current Analysis of Poly-DADMAC Adsorption

Analysis of the amount of cationic polyelectrolyte required to saturate the adsorption capacity of glass fibers was obtained by adding 2.00 g portions of dry C-50-R fibers into 200.0 g of aqueous sodium bicarbonate/sodium sulfate solution that contained 50.0 mg of high-mass poly-DADMAC solids (see earlier description). The mixture was stirred for 10 minutes and then filtered with a mesh screen. The filtrate was evaluated by taking 1000 μ L aliquots and placing them in the cell of a Mutek PCD-03pH streaming current device, along with 15 mL of deionized water. The amount of 1.00 mN polyvinylsulfate, potassium salt, to reach a zero streaming current output was taken as the endpoint of titration. Blank tests were carried out in the same manner, except that no glass fibers were added to the initial solution.

Exposure of Glass Fibers to Polyelectrolytes

Certain of the 400 ml slurry samples, described as “pretreated” in the later discussion, were exposed to high-mass poly-DADMAC at the 0.5% level on glass, based on dry solids. The purpose of this treatment was to change the sign of surface charge of the glass from negative to positive in selected cases. The treatment level was selected to be a small excess over the amount needed to saturate the adsorption capacity of the fiber surfaces. A pipetter was used to add 1.00 ml of 1% high-mass poly-DADMAC (Fisher 40903-0), followed by stirring for 60 seconds. Other than this period of stirring, there was no time delay between the described pretreatment step, when it was included, and subsequent experimental steps.

Two distinct methods were used to deposit mixtures of cationic and anionic polyelectrolytes onto the fiber surfaces. These two approaches will be referred to as “pre-formed complexes” and “*in-situ* mixing,” with complexation presumed to take place in the presence of fibers. The latter method was further differentiated by varying the order of addition.

In the case of pre-formed complexes, volumes of 1% poly-DADMAC and 1% CMC solutions for each test were loaded into a pair of syringes, as shown in Table 1. The mass ratios shown in the table were selected based on charge stoichiometry. A 1:1 charge interaction between the two polyelectrolytes implies a mass ratio of 0.77 parts poly-DADMAC solids per part of CMC, of the type used in the present study. In all cases the total mass of polyelectrolyte was kept constant. In each case, 90 ml of 1000 μ S/cm buffer solution were added to a 200-ml Eberbach blender attachment, which had a small hole cut into its tight-fitting elastic cover. With the Waring blender set to its lowest level, the poly-DADMAC solution was squirted into the aqueous solution, followed 5 seconds later by the CMC solution. Agitation was continued for 30 seconds.

| Table 1. Addition recipes for polyelectrolyte complex formation | | | |
|---|-----------------------------|---|--------------------------------------|
| Charge Ratio (cationic : anionic) | Mass Ratio (dry) | Volume of 1% PolyDADMAC (ml) | Volume of 1% CMC (ml) |
| 0 : 1 | 0:1 | 0.00 | 10.00 |
| 0.3 : 0.7 | 0.231 : 0.7 | 2.48 | 7.52 |
| 0.4 : 0.6 | 0.308 : 0.6 | 3.39 | 6.61 |
| 0.45 : 0.55 | 0.346 : 0.55 | 3.86 | 6.14 |
| 0.5 : 0.5 | 0.385 : 0.5 | 4.35 | 5.65 |
| 0.55 : 0.45 | 0.424 : 0.45 | 4.85 | 5.15 |
| 0.6 : 0.4 | 0.462 : 0.4 | 5.36 | 4.64 |
| 0.7 : 0.3 | 0.539 : 0.3 | 6.42 | 3.58 |
| 1 : 0 | 0.770 : 0.0 | 10.00 | 0.00 |

The mixture, thus formed, was poured promptly into a slurry containing 2.00 g of C-50-R fibers dispersed in 400 mL of the default buffer solution. Two types of mixing equipment were used, depending on the type of data to be collected. For experiments involving determination of adsorbed amounts, the fiber slurry was contained in a Britt Jar apparatus [39], fitted with a 70-mesh screen. The purpose of substituting the coarse screen in place of the default Britt Jar screen was to minimize the likelihood that polyelectrolyte complexes would become filtered by the screen itself. Agitation at 500 rpm. was continued throughout the experiment, except when the jar was empty of aqueous solution. After the polyelectrolytes had been mixing with the fibers for 60 s, the stopcock was opened, and an initial 50 mL of filtrate was discarded. A second aliquot of filtrate was added to the cuvette of a DRT-15CE Turbidimeter from HF Scientific. Average turbidities were obtained from groups of three successive measurements, in which the cuvette was taken out of the instrument and inverted about five seconds before each observation. The procedure used to convert turbidity data to estimates of retention efficiency was the same as has been described earlier [10]. The elapsed time between opening the Britt Jar stopcock and completing all of the turbidity measurements for a given sample was 40 to 60 seconds.

Meanwhile, the filtrate was allowed to slowly drain completely from the Britt Jar. A fresh aliquot of 400 ml default buffer solution was added to the Britt Jar, agitation was promptly resumed, and the solution was again allowed to drain. The damp fibers, were collected from the screen surface, gently squeezed, then placed in tared porcelain cuvettes. The cuvettes and their contents were dried over night at 105 °C in a convection oven, allowed to cool in a desiccator, and then weighed to the nearest 0.3 mg. The cuvettes and

their contents were then heated in a muffle furnace to 450 °C for 60 minutes. Untreated glass fibers did not show any significant change in mass, due to the high-temperature exposure. The difference in the mass before and after heating was used to compute the dry mass of polymer retained on the treated fibers.

The same approach, using the Eberbach blender attachment and the same chemical recipes, was used to prepare samples for analysis of zeta potential (except that no such tests were attempted for experimental conditions involving just one type of polyelectrolyte). Zeta potential data were obtained by means of a micro-electrophoresis, using a Lazer-Zee instrument from PenKem. Solution samples with polyelectrolyte complexes present (as revealed by a turbid appearance) were taken from the previously described procedure and placed in the cell. Four measurements of zeta potential, each involving observation of a field of about 20-200 visible particles, were averaged to obtain the reported data.

A second type of mixing equipment was used for those experiments in which the goal was to determine the effects of treatments on the tensile properties of glass fiber sheets. Using exactly the same volumes and sequences, the fiber slurries were first stirred in a 600 ml plastic beaker with a 5 cm diameter three-lobed impeller blade. Because of the large amounts of dilution water involved in formation of a handsheet, the rinsing step, mentioned earlier, was skipped. Rather, after 60 s of agitation, the contents of the beaker were poured into a partly-filled TAPPI handsheet apparatus [40]. The handsheet procedure was then carried out as specified in the TAPPI method, up to the point of pressing the damp sheet against the screen, using a pair of standard blotter sheets, a metal plate, and two passes of the standard roller. The damp sheets were then dried by

two passes through an Adirondack drum drier, set to 100 °C, with approximately 40 seconds per pass.

In-situ mixing experiments were carried out in a very similar manner as already described, except that 90 mL of additional default buffer solution was added to the initial fiber slurry, making a net volume of 490 mL. In experiments involving either the Britt Jar or impeller stirrer, each titrant was added via syringe, over approximately 1 second, with the two additions spaced about 5 seconds from each other. Thereafter, the experiments continued in identical manner to those in which pre-formed polyelectrolyte complexes were added to the fiber suspension. The elapsed time of contact between the added second polyelectrolytes and the fibers, prior to filtrate collection or sheet-forming, was 60 seconds, matching the elapsed time used in the case of pre-formed complexes.

Physical Tests

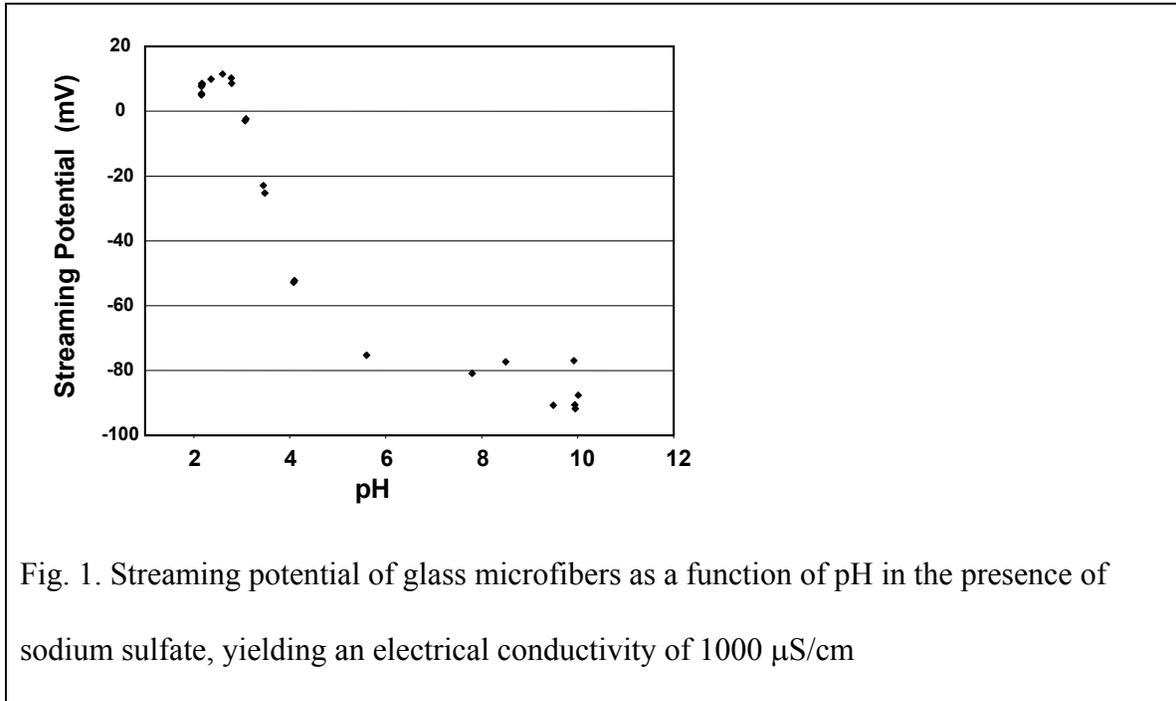
Tensile breaking force analysis was performed with an Instron Model 4411 device, equipped with a ± 500 N static load cell. Before testing, glass-fiber sheet samples were cut into strips 25.4 mm (1.00 inch) wide, and the gap between the grips was set to the 25.4 mm before the start of each test. Subsequent tests all were carried out at neutral pH.

RESULTS AND DISCUSSION

Characterization of Fiber Charge Properties

Figure 1 shows the results of streaming potential tests of the untreated fiber slurry. As has been reported elsewhere [41], the glass fibers showed pH-dependent electrokinetic

behavior. The fact that the potential becomes increasingly negative with increasing pH has been attributed to the progressive dissociation of acidic silanol groups [35].



As shown in Fig. 2, approximately 0.015% addition of poly-DADMAC, based on the amount of glass fiber solids, was sufficient to reach a streaming potential of zero under the default electrolyte conditions of neutral pH and an electrical conductivity of 1000 $\mu\text{S}/\text{cm}$. The endpoint did not depend on molecular mass, over the range tested.

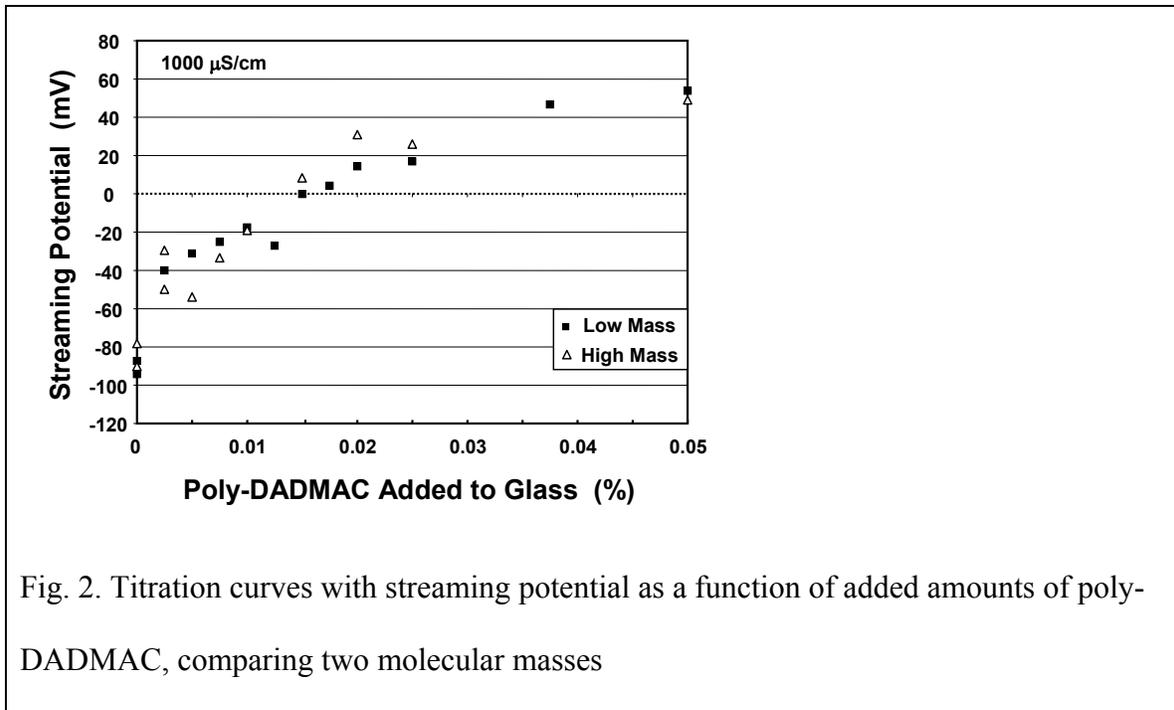


Fig. 2. Titration curves with streaming potential as a function of added amounts of poly-DADMAC, comparing two molecular masses

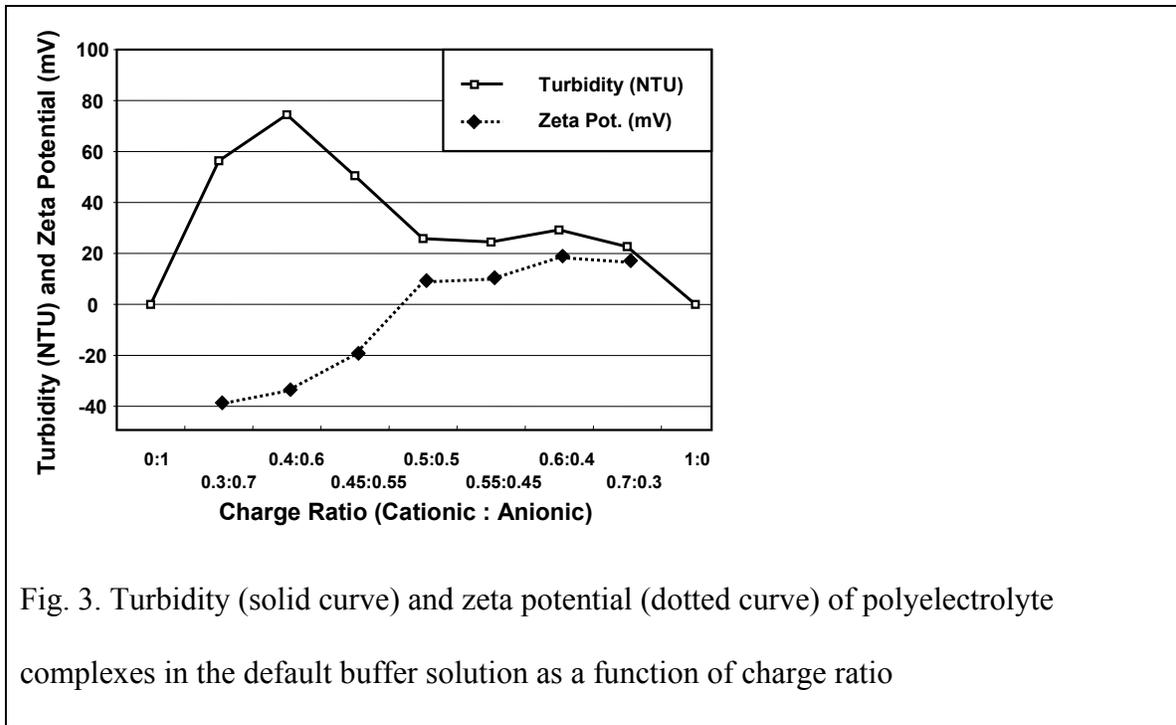
The amount of filtrate collected during successive cycles of the streaming potential analysis was observed to increase by a factor of about 25% due to addition of a small amount of cationic polymer, even at the lowest addition level of poly-DADMAC considered. The enhanced dewatering persisted until the poly-DADMAC addition level exceeded the amount needed to reach zero streaming potential. Thereafter, the amounts of filtrate, collected during successive cycles, gradually decreased back down to the initial value. Related observations have been reported in various studies that involved cationic additives, especially in cases where the molecular masses were lower than about 1 million Daltons [42-44].

Further tests of the same type (not shown) yielded the same titration endpoint when the amount of sodium sulfate was varied. The electrical conductivity range considered in those tests was from 60 to 4800 $\mu\text{S}/\text{cm}$.

Using the streaming current titration method (see Experimental), the saturation level of high-mass poly-DADMAC on the glass fibers was found to be 0.30%. It is worth noting that this value is considerably higher than the endpoint of the streaming potential titrations, as shown in Fig. 2. The difference is attributed to the 100% charged nature of poly-DADMAC, allowing the polyelectrolyte to strongly reverse the net charge associated with the surfaces of substrates to which it becomes adsorbed, long before the substrate has become saturated with adsorbate [45-47].

Polyelectrolyte Complex Preparation and Observations

Figure 3 shows how the turbidity and zeta potential of the polyelectrolyte mixtures, prepared in default buffer solution in the absence of fibers, depended on the charge ratios of the macromolecules. For example, the ratio “0.5:0.5” in the middle of the x-axis indicates equal amounts of positively and negatively charged macromolecular groups, based on the calculated compositions. As expected, charge ratios favoring a net negative charge yielded negative zeta potentials, and *vice versa*.



The turbidity results were somewhat complicated, as was noted earlier [10]. Rather than showing a maximum turbidity at the predicted condition of charge neutrality, the highest turbidity was with a strongly negative mixture, *i.e.* “0.4:0.6.” The complex nature of the turbidity results in Fig. 3 is tentatively attributed to colloidal instability of neutral complexes, causing the solids to gradually collect into particles that are too large to maximize the scattering of light from a defined mass of solids in suspension [48-49]. In particular, the charge-stoichiometric “0.5:0.5” recipe yielded a mixture that tended to form large, settleable particles, leaving the remaining solution clear.

Adsorption of Polyelectrolyte Complexes

As shown in Fig. 4, based on gravimetric analysis, the amount of polyelectrolyte mass retained on the glass fibers depended strongly on the charge ratio and also on the details of how the polymers were applied. Pretreatment of the fibers to make them

cationic was generally favorable to retention of those pre-formed complexes that had a net negative composition, neglecting their counter-ions (unfilled square symbols). By contrast, untreated fibers preferentially retained complexes (whether pre-formed or not) having a near-neutral to positive net charge. Based on the repeatability of individual measurements (plus or minus approx. 0.3 mg), the precision of the absorption determinations was approximately 0.1% of polymer mass on fiber mass.

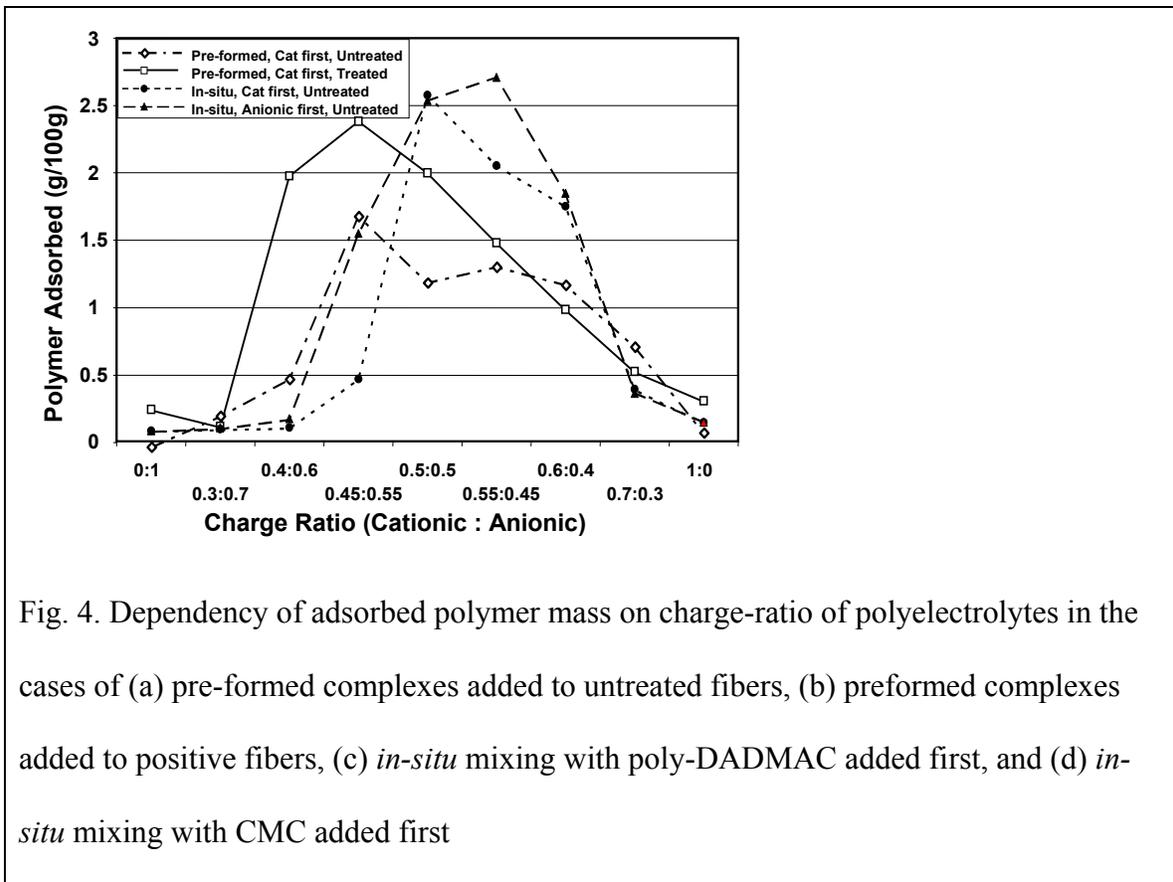


Fig. 4. Dependency of adsorbed polymer mass on charge-ratio of polyelectrolytes in the cases of (a) pre-formed complexes added to untreated fibers, (b) preformed complexes added to positive fibers, (c) *in-situ* mixing with poly-DADMAC added first, and (d) *in-situ* mixing with CMC added first

Some of the highest retention amounts were observed in the cases involving *in-situ* mixing, *i.e.* sequential addition of the polyelectrolytes and presumed *in-situ* formation of complexes (filled symbols). Remarkably, the order of addition of the two

polyelectrolytes did not appear to shift the results in either direction, relative to the effect of charge ratios.

The least efficient adsorption of polyelectrolytes, by far, was observed in the case of pre-formed complexes added to untreated fibers. This observation mirrors some earlier findings when related experiments were carried out with bleached kraft fibers [10]. In that case it was found that pre-treatment, giving the fibers a positive charge, improved the retention efficiency of pre-formed complexes, regardless of their charge ratio. Those results were rationalized in terms of the relatively low anionic charge density of cellulosic surfaces, compared to the stronger positive charge of the treated fibers. It was hypothesized that fibers having a higher charge density would be better able to interact with oppositely charged “patches” on the freshly-formed complexes. The present results, involving more highly charged glass fiber surfaces, suggest that further refinement of the hypothesis is needed. It is also worth noting a study by Buchhammer *et al.* [48], which showed contrasting results for sequential addition *vs.* pre-mixing of oppositely charged polyelectrolytes, with measurements of their adsorption onto silica. The cited study was different from the present work, since the solid phase was rinsed free of excess, unadsorbed polyelectrolyte after exposure to the first (cationic) polyelectrolyte; such a step minimizes the possibility of subsequent complex formation in solution upon later addition of the second polymer.

Results shown in Fig. 4 for pre-formed complex adsorption onto untreated glass fibers are in contrast to earlier work reported by Kekkonen *et al.* [28]. Those researchers observed essentially zero adsorption onto silica wafers that were exposed to polyelectrolyte complexes having a net negative charge. Though it is true that the cited

work involved a different type of anionic polyelectrolyte – possibly explaining the difference in results – it seems most likely that the proper explanation involves the different substrate geometries and flow patterns. Earlier studies have shown more favorable deposition of colloidal matter onto small fibers or fibrils, compared to deposition onto flat substrates of similar composition [50]. Particles in suspension that approach each other, due to effects of hydrodynamic shear, have a tendency to avoid direct contact, due to the viscosity of the intervening liquid [51-52]. In addition, hydrodynamic forces might be able to detach polyelectrolyte complexes from flat substrates, as used in the cited study [53]. By contrast, a complex that becomes wrapped around a fiber would be more difficult to detach, as in the case of gum that gets tangled in hair.

Results of turbidimetric analyses (not shown) indicated the same retention trends as the gravimetric analysis, although the latter method was judged to be more precise. Thus, pretreatment of the fibers, to give them an initial positive charge, had a dramatic effect in improving the retention efficiency of those pre-formed complexes having a net negative charge (as shown in Fig. 3). Again, similar to the trends shown in Fig. 4, the untreated (initially negatively charged) fibers resulted in maximum retention of those pre-formed complexes that had a moderately positive zeta potential.

Strength of Glass-Fiber Sheets

Results of tensile tests, shown in Fig. 5, indicated a strong dependency on charge ratio in the absence of fiber pre-treatment. The logarithmic scale of the vertical axis reveals that the strength increased by a factor of up to about 200 due to some of the

polymer treatments. Replicate tests of strips taken from the same handsheets were highly reproducible, especially in the case of sheets that showed substantial effects due to the polymers. Relative standard deviations of the breaking force, based on linear quantities, were consistently within the range of zero to 7% in the case of the stronger samples. The weakest samples, including blanks prepared without any polymer addition, yielded relative standard deviations in the range 10 to 20%.

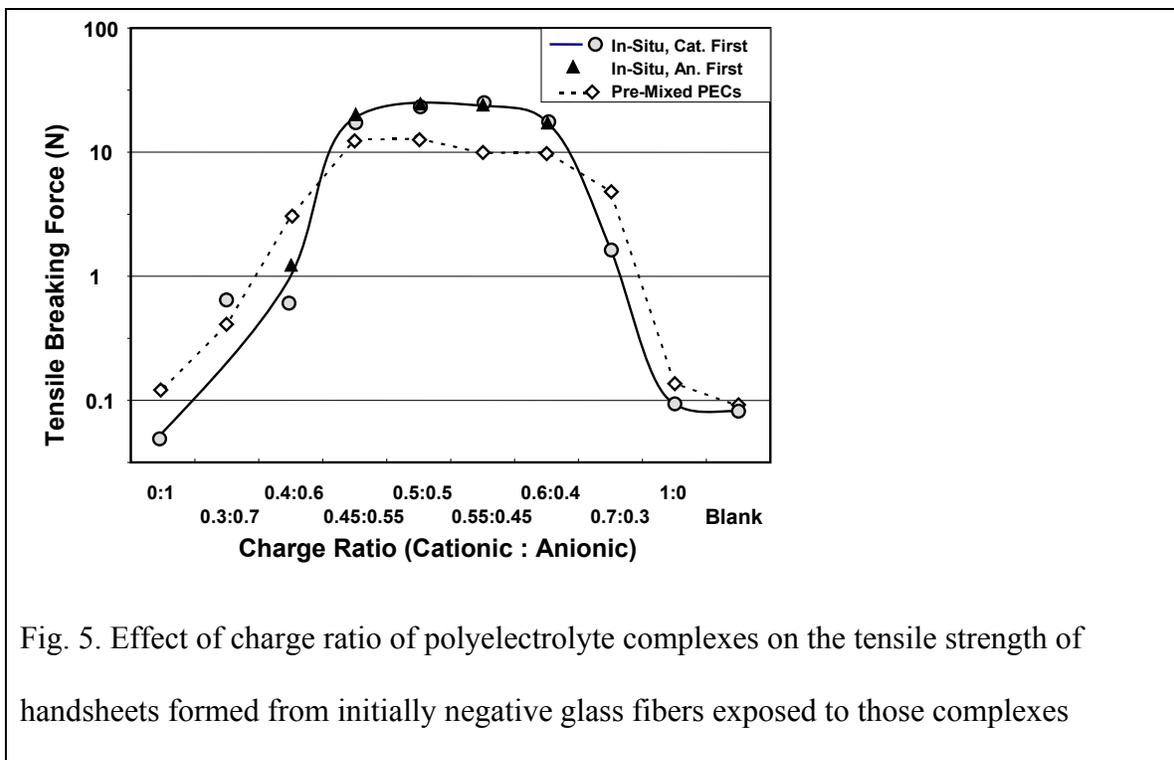


Fig. 5. Effect of charge ratio of polyelectrolyte complexes on the tensile strength of handsheets formed from initially negative glass fibers exposed to those complexes

The flat “plateau” at the top of each curve has potential importance relative to feasibility of polyelectrolyte complex deposition at an industrial scale. In principle, it would make sense to control a process so that it always stays within such a plateau region, regardless of process variations.

Compared to in-situ mixing of the polyelectrolytes (both orders of addition represented by the solid curve), addition of pre-formed complexes (dotted line) yielded substantially lower strength within the favorable range of charge ratios. In general, there was an approximate factor of two strength advantage of *in-situ* treatment under these ideal treatment conditions.

It was hypothesized that maybe the lower effectiveness of the pre-formed complexation strategy was due to aging of the complexes, leading to denser, less hydrated precipitates. To evaluate this hypothesis, tests with the “0.5:0.5” condition were repeated, with ten minutes of delay time before addition of the mixture to the fiber slurry. In one case the pre-formed complexes were allowed to settle for ten minutes, and in another case they were stirred magnetically throughout the period. Results given in Table 2 generally support the hypothesis. However, it is noteworthy that brisk agitation appeared to keep the complexes in a finely divided form, which gave better strength efficiency, compared to the large precipitates that formed in the unstirred sample.

| Table 2. Effect of Aging of Pre-Formed Complexes | | |
|---|---|----------------------------|
| Condition | Appearance of Polymer Mixture | Tensile Breaking Force (N) |
| Default conditions, no delay in adding the polyelectrolyte mixture | Turbid, fine-grained | 12.8 |
| Polyelectrolyte mixture stirred briskly for ten minutes before addition to the fibers | Turbid, fine-grained | 10.8 |
| Polyelectrolyte mixture allowed to sediment for ten minutes before addition | Large particles suspended in clear solution | 7.1 |

Figure 6 compares the two sets of experiments in which pre-formed polyelectrolyte complexes were added to glass fibers, focusing on the effect of pretreatment of the fibers. Remarkably, pretreating the fibers to make them cationic yielded a strong advantage, relative to adding the complexes to untreated fibers, only when the complexes were strongly negative in net composition. Strength results in the case of initially negative fibers were much more promising than would have been predicted based on the adsorbed amounts shown in Fig. 4. A possible contributing factor that might be used to rationalize these differences involves the relatively low hydrodynamic shear used in formation of a handsheet, compared to the continuous stirring at 500 rpm. during the Britt jar experiment. Such a difference would be expected to reduce the advantage of a system yielding stronger attachments of polymer complexes to fiber surfaces.

It is worth noting that the results shown in Fig. 6 are in apparent conflict with earlier experiments involving cellulosic fibers [10]. Those tests showed a strength advantage of cationic pretreatment of the fibers, regardless of the charge ratio used in preparing polyelectrolyte complexes. It is reasonable that the higher charge density of glass, relative to the recycled kraft fibers used in the earlier study, should result in stronger binding of polyelectrolyte complexes that possess strongly cationic areas facing outwards.

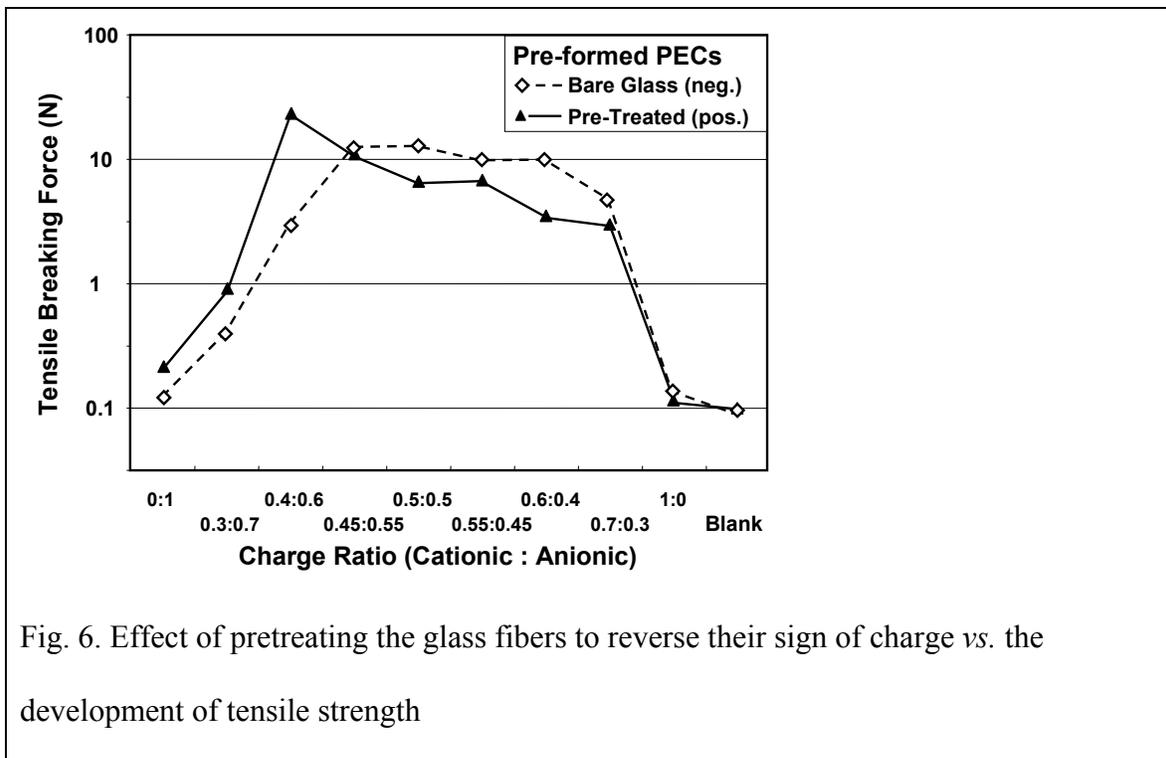


Fig. 6. Effect of pretreating the glass fibers to reverse their sign of charge vs. the development of tensile strength

A key concern, when developing chemical strategies for implementation in a broad range of papermaking operations, is that positive results might be limited to a narrow range of electrolyte conditions. In particular, studies have shown that levels of salt can affect the performance of polyelectrolytes in various aspects of papermaking [54-56]. Table 3 shows the results of tests in which *in-situ* mixing of polyelectrolytes was carried out at different levels of sodium sulfate. The poly-DADMAC was the first additive, the charge ratio was “0.5:0.5,” and the glass fibers were initially in their negative charge state. As shown, the treatment was ineffective in the absence of added sodium sulfate, whereas the system appeared to be tolerant of high salt levels. The poor performance of the complexes in the absence of added salt can be rationalized in terms of studies showing lesser amounts of adsorbed polymer under such conditions [49,52]. The continued high performance at very high salt levels is contrary to expectations based on

adsorption of individual polyelectrolytes [54,57], though the predictions of the cited studies would not necessarily apply in the case of polyelectrolyte complexes.

| Table 3. Effect of Salt on Strength Results by <i>In-Situ</i> Mixing | | |
|--|---|----------------------------|
| Condition | Electrical conductivity ($\mu\text{S}/\text{cm}$) | Tensile Breaking Force (N) |
| Sodium bicarbonate only | 60 | 0.75 |
| Default buffer solution | 1000 | 25 |
| Extra 1 ml of 5% Na_2SO_4 | 1300 | 25 |
| Extra 10 ml 5% Na_2SO_4 | 3700 | 27 |

A remaining question to consider concerns how far is it possible to push the concept of polyelectrolyte complex deposition, to achieve superior strength results. Figure 7 shows the results of *in-situ* mixing tests in which the charge ratio of the complexes was kept at the 1:1 stoichiometric level, and the poly-DADMAC was always added in advance of the CMC to a suspension of untreated fibers. The horizontal axis shows the net amount of polyelectrolytes added (not necessarily retained). What is especially notable about these results is that the curve continues to climb strongly up to a level of 10% polyelectrolyte added to fiber. To place these results in context, the benefits of adding strength additives, such as cationic starch, to cellulosic fibers usually reach a plateau at about 1% by mass, or somewhat higher [17-18,54]. Recently, however, it was shown that substantially higher amounts of starch could be retained and contribute to

higher strength, when added in sequence with an oppositely charge polymer [22-23,58].

In light of the present work, it is reasonable to expect that the cited work may involve deposition of polyelectrolyte complexes as a mechanism of strength development.

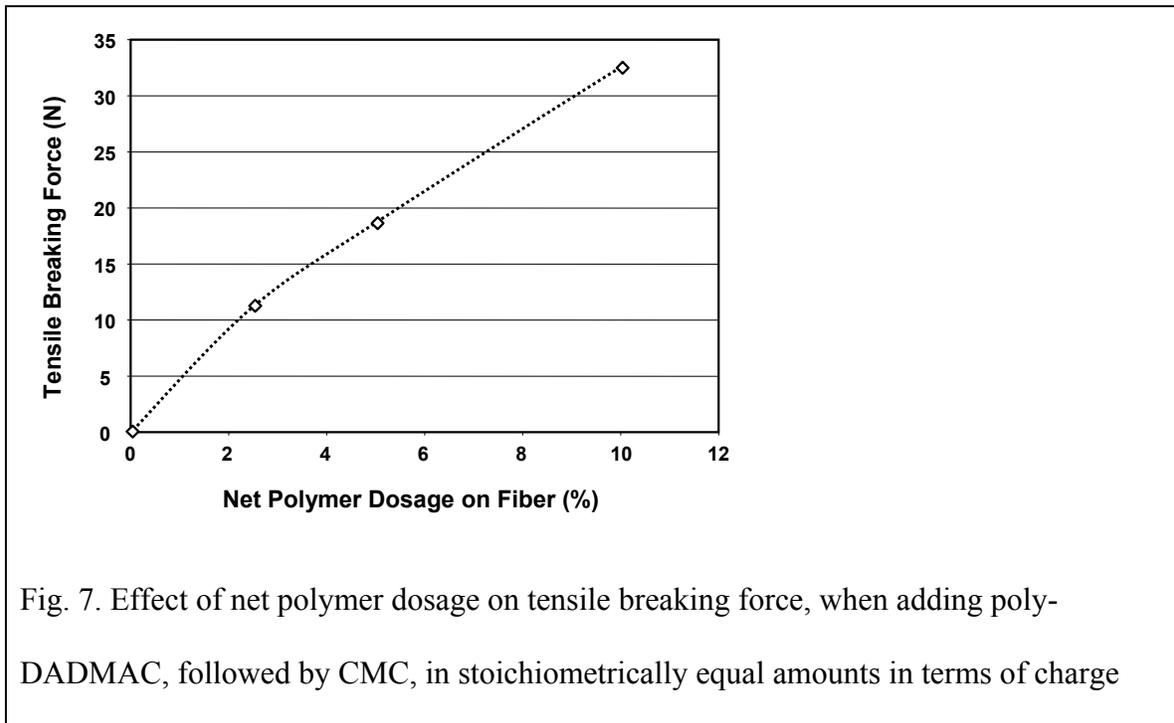


Fig. 7. Effect of net polymer dosage on tensile breaking force, when adding poly-DADMAC, followed by CMC, in stoichiometrically equal amounts in terms of charge

A line of inquiry left unanswered by the present work involves whether some of the results may be affected by distributions in the molecular mass of the polyelectrolytes. In particular, commercially available poly-diallyldimethylammonium chloride has been found to have a broad mass distribution [59]. It would be expected that lower-mass molecules within a mixture would tend to diffuse more quickly onto fiber surfaces, but that these early arrivals might be displaced by higher-mass molecules, arriving later. These issues can be expected to be important in papermaking systems, since the time between polymer addition and sheet formation often is a matter of seconds, whereas a number of minutes may be required for polyelectrolyte adsorption to approach

a quasi-equilibrium level [33]. Also it would be of interest to find out whether a polyelectrolyte complex can effectively compete for adsorption sites vs. uncomplexed macromolecules in the same mixture. Such questions might be considered in future studies.

CONCLUSIONS

1. Glass microfibers were judged to be a useful model material for evaluating colloid-chemical mechanisms related to papermaking science. The fibers were easy to disperse, easy to form into handsheets of high uniformity, very convenient for gravimetric determination of polymer adsorbed amounts, and ideal for evaluation of the contributions of polyelectrolytes to inter-fiber bonding.
2. Polyelectrolyte complexes having charge stoichiometry ratios in the range of 2:3 to 3:2 generally yielded the highest efficiencies of adsorption onto glass fibers, and also the highest tensile breaking force of the resulting dried sheets. Within this range of charge ratios, results were strongly affected by the initial sign of charge of the fibers. Pretreatment of the fibers with poly-DADMAC to make them positive yielded preferential retention of polyelectrolyte complexes having a net negative charge. By contrast, fibers having a net negative surface preferentially retained complexes having a net positive charge.
3. In terms of strength development, sequential addition of the oppositely charged polyelectrolytes and presumed *in-situ* formation of polyelectrolyte complexes was more effective than addition of pre-formed complexes. These results were consistent

with follow-up tests showing that the effectiveness of pre-formed complexes, in terms of strength development, decreased if there was a delay before their addition to the fiber slurry.

4. Salt was essential for the observed strength development. The two-polymer treatment yielded relatively little bonding strength in the absence of sodium sulfate. By contrast, there was no further significant effect on strength development when the electrical conductivity was varied within the range of 1000 to 3700 $\mu\text{S}/\text{cm}$ by addition of more sodium sulfate.

REFERENCES

1. ERSPAMER, A., "The Flocculation and Dispersion of Papermaking Fibers," *Paper Trade J.* 110(24):33-38 (1940).
2. WÅGBERG, L., and LINDSTÖM, T., "Some Fundamental Aspects on Dual-Component Retention Aid Systems," *Nordic Pulp Paper Res. J.* 2(2):49-55 (1987).
3. PETZOLD, G., "Dual-Addition Schemes," in *Colloid-Polymer Interactions*, Farinato, R. S., and Dubin, P. L., Eds., Ch. 3, 83-100, Wiley-Interscience, New York, 1999.
4. CHAN, L.-L., "Dry Strength Resins: Useful Tools for Paper Making," *Pulp Paper Can.* 77(6):T93-95 (1976).
5. CARR, M. E., HAMERSTRAND, G. E., HOFREITER, B. T., and RUSSELL, C. R., "A Polysalt Complex for Wet-End Addition," *Tappi* 60(12):148-149 (1977).
6. NEALEY, L., HAMADA, M., and KIMURA, Y., "Some Factors Affecting Strength Enhancement by a Polyacrylamide Dual Polymer System," TAPPI Papermakers Conf., 261-268 (1989).
7. HUBBE, M. A., JACKSON, T. L., and ZHANG, M., "Fiber Surface Saturation as a Strategy to Optimize Dual-Polymer Dry-Strength Treatment," *Tappi J.* 2(11):7-12 (2003).
8. WATANABE, M., GONDO, T., and KITAO, O., "Advanced Wet-end System with Carboxymethyl-cellulose," *Tappi J.* 3(5):15-19 (2004).
9. WU, Z., CHEN, S., and Lu, Y., "Investigation on Mechanisms of the Complexes of Starch and Poly-(diallyldimethylammonium chloride) as a Dry Strength Agent," 2nd ISTPPBFP, Nanjing, China, 2004.
10. HUBBE, M. A., MOORE, S. M., and LEE, S. Y., "Effects of Charge Ratios and Cationic Polymer Nature on Polyelectrolyte Complex Deposition onto Cellulose," *Indust. Eng. Chem. Res.* 44(9):3068-3074 (2005).
11. GERNANDT, R., WÅGBERG, L., GÄRD Lund, L., and DAUTZENBERG, H., „Polyelectrolyte Complexes for Surface Modification of Wood Fibers. I. Preparation

- and Characterization of Complexes for Dry and Wet Strength Improvement of Paper,” *Colloids Surf. A* 213(1):15-25 (2003).
12. GÄRDLUND, L., WÅGBERG, L., and GERNANDT, R. “Polyelectrolyte Complexes for Surface Modification of Wood Fibers. II. Influence of Complexes on Wet and Strength Strength of Paper,” *Colloids Surf. A* 218(1-3):137-149 (2003).
 13. GÄRDLUND, L., FORSSTRÖM, J., ANDREASSON, B., and WÅGBERG, L., *Nordic Pulp Paper Res. J.* 20(1):71-77 (2005).
 14. PHILIPP, B., DAUTZENBERG, H., LINOW, K.-J., KÖTZ, J., and DAWYDOFF, W., “Polyelectrolyte Complexes – Recent Developments and Open Problems,” *Prog. Polym. Sci.* 14(1):91-172 (1989).
 15. OERTEL, U., PETZOLD, G., BUCHHAMMER, H., GEYER, S., SCHWARZ, S., MÜLLER, U., and RÄTZSCH, M., “Introduction of Surface Charge into Polymers by Polyelectrolyte Complexes,” *Colloids Surf.* 57(3-4):375-381 (1991).
 16. PETZOLD, G., NEBEL, A., BUCHHAMMER, H.-M., and LUNKWITZ, K., “Preparation and Characterization of Different Polyelectrolyte Complexes and their Application as Flocculants,” *Colloid Polym. Sci.* 276(2):125-130 (1998).
 17. ROJAS, O. J., and NEUMAN, R. D., “Adsorption of Polysaccharide Wet-End Additives in Papermaking Systems,” *Colloids Surf. A* 155(2-3):419-432 (1999).
 18. HUBBE, M. A., VENDITTI, R. A., BARBOUR, R. L., and ZHANG, M., “Changes to Unbleached Kraft Fibers due to Drying and Recycling,” *Prog. Paper Recycling* 12(3):11-20 (2003).
 19. BAKER, C. F., “Good Practice for Refining the Types of Fiber Found in Modern Paper Furnishes,” *Tappi J.* 78(2):147-153 (1995).
 20. LINDSTRÖM, T. and FLORÉN, T., “The Effects of Cationic Starch Wet End Addition on the Properties of Clay Filled Papers,” *Svenk Pappersitdn.* 87(12):R99-104 (1984).
 21. FORMENTO, J. C., MAXIMINO, M. G., MINA, L. R., SRAYH, M. I., and MARTINEZ, M. J., “Cationic Starch in the Wet End: Its Contribution to Interfiber Bonding,” *Appita* 47(4):305-308 (1994).
 22. BROUWER, P. H., “Anionic Wet-End Starch In – Size-Press Out?” *Wochenbl. Papierfabr.* 125(19):928-937 (1997).
 23. WIELEMA, T. A., and BROUWER, P. H., “Paper Performance and the Increased Use of Fillers and Pigments,” *Paper Technol.* 44(9):27-40 (2003).
 24. SMITH, D. C., “Chemical Additives for Improved Compression Strength of Unbleached Board,” *TAPPI Papermakers Conf.*, 393-404 (1992).
 25. MAXIMOVA, N., LAINE, J., and STENIUS, P., “Adsorption of Lignin-Cationic Starch Complexes on Cellulose Fibers and their Effect on Sheet Properties,” *Paperi Puu* 87(3):176-182(2005).
 26. WÅGBERG, L., FORSBERG, S., JOHANSSON, A., and JUNTTI, P., “Engineering of Fiber Surface Properties by Application of Polyelectrolyte Multilayer Concept. Part 1. Modification of Paper Strength,” *J. Pulp Paper Sci.* 28(7):222-228 (2002).
 27. DECHER, G., “Fuzzy Nanoassemblies: Toward Layered Polymeric Multicomposites,” *Science* 277(5330):1232-1237 (1997).
 28. KEKKONEN, J., LATTU, H., and STENIUS, P., “Adsorption Kinetics of Complexes Formed by Oppositely Charged Polyelectrolytes,” *J. Colloid Interface Sci.* 234(2):384-392 (2001).

29. CHEN, J., HEITMANN, J. A., and HUBBE, M. A., "Dependency of Polyelectrolyte Complex Stoichiometry on the Order of Addition. 1. Effect of Salt Concentration during Streaming Current Titrations with Strong Poly-acid and Poly-base," *Colloids Surf. A.* 223(1-3):215-230 (2003).
30. CHEN, J., HUBBE, M. A., HEITMANN, J. A., ARGYROPOULOS, D. S., and ROJAS, O. J., "Dependency of Polyelectrolyte Complex Stoichiometry on the Order of Addition. 2. Aluminum Chloride and Poly-vinylsulfate," *Colloids Surf. A.* 246(1-3):71-79 (2004).
31. CUNDALL, R. B., LAWTON, J. B., and MURRAY, D., "Polyelectrolyte Complexes, 1. The Effect of pH and Ionic Strength on the Stoichiometry of Model Polycation – Polyanion Complexes," *Makromol. Chem.* 180(12):2913-2922 (1979).
32. KABANOV, V. A., ZEZIN, A. B., IZUMRUDOV, V. A., BRONICH, T. K., and BAKEEV, K. N., "Cooperative Interpolyelectrolyte Reactions," *Makromol. Chem. Suppl.* 13:137-155 (1985).
33. ÖDBERG, L., TANAKA, H., and SWERIN, A., "Kinetic Aspects of the Adsorption of Polymers on Cellulosic Fibers," *Nordic Pulp Paper Res. J.* 8(1):6-9,47 (1993).
34. FORSBERG, S., and STRÖM, G., "The Effect of Contact Time Between Cationic Polymers and Furnish on Retention and Drainage," *J. Pulp Paper Sci.* 20(3):J71-75 (1994).
35. ILER, R. K., *The Chemistry of Silica – Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*, Wiley, New York, 1979.
36. FERNANDEZ-DINIZ, J. M. B., "Charge-pH Isotherms of Paper Wood Pulps," *Holzforschung* 50(1):37-41 (1996).
37. WANG, F., and HUBBE, M. A., "Charge Properties of Fibers in the Paper Mill Environment. Part 1. Effect of Electrical Conductivity," *J. Pulp Paper Sci.* 28(10):347-353 (2002).
38. WANG, F., and HUBBE, M. A., "Development and Evaluation of an Automated Streaming Potential Measurement Device," *Colloids Surf. A* 194(1-3):221-232 (2001).
39. BRITT, K. W., "Mechanisms of Retention during Paper Formation," *Tappi* 56(10):46-50 (1973).
40. TAPPI Method T205, TAPPI Test Methods, TAPPI Press, Atlanta, 1996.
41. VERNHET, A., BELLONFONTAINE, M. N., and DOREN, A., "Comparison of 3 Electrokinetic Methods to Determine the Zeta-Potential of Solid Surfaces," *J. Chem. Phys. Physico-Chem. Biolog.* 91(11-12):1728-1747 (1994).
42. DAVISON, R. W., and CATES, R. E., "Electrokinetic Effects in Papermaking Systems: Theory and Practice," *Paper Technol. Ind.* 16(2):107-114 (1975).
43. HORN, D., and MELZER, J., "Influence of Macromolecular Cationic Drainage Aids on Electrokinetic Properties of Pulp," *Papier* 29(12):534-541 (1975).
44. POPPEL, E., "The Role of Zeta Potential in Some Wet-End Processes and their Optimization by Electrokinetic Control," *Wochenbl. Papeirfabr.* 120(14):565-571 (1992).
45. BAUER, D., KILLMANN, E., and JAEGER, W., "Flocculation and Stabilization of Colloidal Silica by the Adsorption of Poly-diallyldimethylammonium chloride (PDADMAC) and of Copolymers of DADMAC and *N*-methyl-*N*-vinylacetamide (NMVA)," *Colloid Polym. Sci.* 276(8):698-708 (1998).

46. SCHWARZ, S., BUCHHAMMER, H.-M., LUNKWITZ, K., and JACOBASCH, H.-J., "Polyelectrolyte Adsorption on Charged Surfaces: Study by Electrokinetic Measurements," *Colloids Surf. A* 140(1-3):377-384 (1998).
47. SCHLENOFF, J. B., and DUBAS, S. T., "Mechanism of Polyelectrolyte Multilayer Growth: Charge Overcompensation and Distribution," *Macromol.* 34(3):592-598 (2001).
48. BUCHHAMMER, H.-M., MENDE, M., and OELMANN, M., "Formation of Mono-Sized Polyelectrolyte Complex Dispersions: Effects of Polymer Structure, Concentration, and Mixing Conditions," *Colloids Surf. A* 218(1-3):151-159 (2003).
49. MENDE, M., BUCHHAMMER, H. M., SCHWARZ, S., PETZOLD, B., and JAEGER, W., "The Stability of Polyelectrolyte Complex Systems of Poly(diallyldimethylammonium chloride) with Different Poly-anions," *Macromol. Symp.* 221:121-133 (2004).
50. HASLAM, J. H., and STEELE, F. A., "The Retention of Pigments in Paper," *Tech. Assoc. Papers* 19:249-252 (1936).
51. ADAMCZYK, Z., and VAN DE VEN, T. G. M., "Kinetics of Particle Accumulation at Collector Surfaces. 1. Approximate Analytical Solutions," *J. Colloid Interface Sci.* 97(1):68-90 (1984).
52. ADAMCZYK, Z., DABROS, T., CZARNECKI, J., *et al.*, "Kinetics of Particle Accumulation at Collector Surfaces. 2. Exact Numerical Solutions," *J. Colloid Interface Sci.* 97(1):91-104 (1984).
53. HUBBE, M. A., "Theory of Detachment of Colloidal Particles from Flat Surfaces Exposed to Flow," *Colloids Surf.* 12(12):151-178 (1984).
54. VAN DE STEEG, H. G. M., DE KEIZER, A. D., COHEN STUART, M. A., and BIJSTERBOSCH, B. H., "Adsorption of Cationic Starches on Microcrystalline Cellulose," *Nordic Pulp Paper Res. J.* 8(1):34-40 (1993).
55. BEAUDOIN, R. GRATTON, R., and TURCOTTE, R., "Performance of Wet-End Cationic Starches in Maintaining Good Sizing at High Conductivities in Alkaline Fine Paper," *J. Pulp Paper Sci.* 21(7):J238-243 (1995).
56. BUONTEMPO, J. T., SHERMAN, L. M., and ST. JOHN, M. R., "Effects of Salts on the Performance of Cationic Flocculants Used as Retention Aids for Alkaline Fine Paper," *Papermakers Conf.*, 49-58, TAPPI Press, Atlanta, 1996.
57. SUKHISHVILI, S. A., and GRANICK, S., "Polyelectrolyte Adsorption onto an Initially-Bare Solid Surface of Opposite Electrical Charge," *J. Chem. Phys.* 109(16):6861-6868 (1998).
58. HEATH, D., ERNST, A. J., HOFREITER, B. T., PHILLIPS, B. S., and RUSSEL, C. R., "Flocculating Agent-Starch Blends for Interfiber Bonding and Filler Retention: Comparative Performance with Cationic Starches," *Tappi* 57(11):109-111 (1974).
59. SWERIN, A., and WÅGBERG, L., "Size-Exclusion Chromatography for Characterization of Cationic Polyelectrolytes Used in Papermaking," *Nordic Pulp Paper Res. J.* 9(1):18-25 (1994).

Figure Captions

Fig. 1. Streaming potential of glass microfibers as a function of pH in the presence of sodium sulfate, yielding an electrical conductivity of 1000 $\mu\text{S}/\text{cm}$

Fig. 2. Titration curves with streaming potential as a function of added amounts of poly-DADMAC, comparing two molecular masses

Fig. 3. Turbidity (solid curve) and zeta potential (dotted curve) of polyelectrolyte complexes in the default buffer solution as a function of charge ratio

Fig. 4. Dependency of adsorbed polymer mass on charge-ratio of polyelectrolytes in the cases of (a) pre-formed complexes added to untreated fibers, (b) preformed complexes added to positive fibers, (c) *in-situ* mixing with poly-DADMAC added first, and (d) *in-situ* mixing with CMC added first

Fig. 5. Effect of charge ratio of polyelectrolyte complexes on the tensile strength of handsheets formed from initially negative glass fibers exposed to those complexes

Fig. 6. Effect of pretreating the glass fibers to reverse their sign of charge *vs.* the development of tensile strength

Fig. 7. Effect of net polymer dosage on tensile breaking force, when adding poly-DADMAC, followed by CMC, in stoichiometrically equal amounts in terms of charge