Fiber Surface Saturation as a Strategy to Optimize Dual-Polymer Dry Strength Treatment

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ABSTRACT

The compression strength of unbleached kraft handsheets was maximized when the first component of a dual-polymer treatment was added at a level corresponding to saturation of the fiber surface. The saturation level of poly-diallyldimethylammonium chloride (poly-DADMAC), determined by streaming current analysis, also coincided with a maximum in water retention value (WRV) and a minimum in the light scattering coefficient of the paper. Idealized descriptions of the polymer interactions are proposed to explain the observations.

INTRODUCTION

Polymeric wet-end additives are becoming increasingly used to meet customer requirements for the dry strength of paper [1-6]. The increased use of such chemicals is due, in part, to declines in fiber quality, especially when fibers are recycled one or more times. Many studies have quantified the adverse effect of paper drying on the subsequent bonding ability of the recycled fibers [6-14].

Reduced bonding ability of fibers leaves the papermaker with difficult choices. The option of increasing basis weight to meet the strength specifications is wasteful; it requires greater usage of raw material, increased energy to dry the paper, and increased expense to ship the heavier product [15-16]. Extensive refining, in an effort to restore bonding ability to recycled kraft pulp, results in increased fiber fines and slower drainage [17-18].

The beneficial effects of cationic starch [16,19-21] and other wet-end dry-strength additives [1-6,22-25] are well known. In particular, dual-polymer dry strength programs can yield significant strength benefits [26-31]. Typically a cationic additive is followed by anionic acrylamide copolymer, carboxymethyl cellulose

(CMC), or starch [4,6,27,29,32]. Due to the cost of these chemicals it is important to establish the principles underlying their most efficient use.

Theories of Paper Strength

Paper's strength can be attributed to the strength of individual fibers and the strengths of the bonds formed between them [33]. Tensile or compressive failure of typical paperboard grades involves primarily the failure inter-fiber bonds, with a lesser degree of fiber breakage [33-34]. Inter-fiber bonding depends, in turn, on the relative bonded area, and the strength of those bonds per unit of bonded area [33]. One might imagine polymeric dry-strength additives filling in spaces between adjacent fiber surfaces to increase the bonded area. However, research results suggest otherwise. For instance, cationic starch appears mainly to increase strength per unit of bonded area [20,35-36].

Dual-polymer dry-strength treatments appear to involve an anchoring mechanism. For instance, addition of CMC, an anionic dry-strength polymer, to a slurry of untreated kraft pulp gave very little strength improvement [6]. By contrast, strength benefits due to CMC were observed both in the primary sheets and in recycled paper when the fibers had been pre-treated with a highly cationic poly-electrolyte. Earlier work showed that balancing of colloidal charges can be important in the optimization of such a dual treatments [1,26-27].

Hypothesis

It is proposed that the effectiveness of a dual-polymer dry-strength treatment should depend on the dosage of a highly charged, linear polymer used as the first additive.

The rationale behind this hypothesis is shown in Fig. 1. Consider three levels of cationic polymer addition to a slurry of fibers that initially have a net negative surface charge. In case "A" the addition level is well below that which would saturate the fiber surface. In case "B" the amount equals an adsorption maximum, *i.e.* a condition of saturation. In case "C" there is an excess, and some cationic polymer remains in solution after a defined period of mixing.

Past research supports case "A", as follows: Highly charged, cationic polymers at sufficiently low salt concentrations adsorb with high affinity onto negatively charged surfaces [37-38]. Little remains in solution after mixing and equilibration, as long as bare areas of surface remain. In the presence of turbulent flow only a small fraction of a second is needed for most polymers to have collided with a surface [39-40]. If there is sufficient space available, evidence suggests that highly charged, linear polymers will tend to lie down flat [40-42].

Part "B" of Fig. 1 is consistent with polyelectrolytes' tendency to continue to adsorb from aqueous solution onto surfaces of opposite charge well beyond the

point at which the net surface charge has been satisfied [43-46]. New evidence supporting this view comes from studies of self-assembled multi-layers of oppositely charged polyelectrolytes [46-48]. These studies reveal that the outermost layer of polyelectrolytes usually has loops and tails extending outwards towards the bulk solution. The fiber surface, too, has a layer of hemicellulosic and cellulosic polymers extending outwards [49-50]. The three-dimensional nature of these polymer layers helps to explain why exposure of a wetted surface to an excess of oppositely charged polymer ordinarily reverses the zeta potential [47]. A similar mechanism explains why adsorption of cationic polymer on fibers to be maximized at a low density of polymer charge [51].

Recent work [52] suggests that a suitably high amount of cationic polymers adsorbed at a fiber surface can inhibit the tendency of those polymers to spread out and lie down. This is another factor that helps to support the reasonableness of case "B". This mechanism is expected to work in cases where the rate at which molecules arrive at the surface (related to their concentration) is high enough relative to their rate of conformational change (related to their molecular mass) [38-39].

Figure 2 provides an idealized view of how subsequent addition of an anionic polyelectrolyte is likely to affect the three cases considered in Fig. 1. In case "A" the adsorbed cationic polymers provide anchoring sites for the anionic polymers. It is reasonable to expect that case "B", with loops and tails of cationic polymer extending from the surface, should lead to a maximum adsorbed amount of anionic polymer, though proof of this concept lies beyond the present work. In case "C", where there is an excess of cationic polymers in solution, subsequent addition of anionic polymer is expected to result in formation of polyelectrolyte complexes. Past work suggests that pre-formed polyelectrolyte complexes can be used as flocculants [53-54], though their dry strength effects have not been well studied. In preliminary work addition of poly-diallyldimethylammonium chloride (poly-DADMAC), followed by carboxymethylcellulose (CMC) increased dry strength, whereas addition of a pre-mixed complex of the oppositely charged polyelectrolytes did not.

To test the hypothesis, it was necessary first to determine the saturation level corresponding to case "B" in Fig. 1. The procedure used was based on previous work [55-57]. Briefly stated, one adds a known excess of cationic polymer solution to a fiber slurry with standardized mixing and equilibration time, followed by filtration. Excess cationic polymer in an aliquot of filtrate is back-titrated to a neutral endpoint, and the adsorbed amount is calculated.

EXPERIMENTAL

Materials

Unbleached softwood kraft pulp from the Mansfield, LA mill of International Paper was de-shived, centrifuged, and refrigerated until use. For tests aimed at quantifying effects of drying, pulp was refined to 426 ml CSF, using a PFI mill and paper was made without chemical treatment. To quantify effects of dry-strength chemicals, the pulp was refined to approximately 400 ml CSF, then centrifuged without further refining. The resulting freeness was 615 ml CSF. The higher freeness and low fines content was expected to amplify the relative effects of the chemical additives.

Polyelectrolyte solutions were prepared in deionized water. The cationic polymer was Alcofix® 169, a poly-diallyldimethylammonium chloride (poly-DADMAC) product from Ciba Specialty Chemicals. The carboxymethylcellulose was CMC 7M from Hercules, Inc. The anionic titrant was 0.0025 N poly-(vinylsulfate potassium salt) solution (PVSK) from Ondeo Nalco.

Streaming Current Analysis

Streaming current titrations were performed with an ECA 2000 from Chemtrac Systems. The poly-DADMAC concentration was calibrated by titration with PVSK [58].

Analyses of polymer adsorption onto fiber were performed with 0.6% consistency pulp. Different amounts of 0.4% by mass poly-DADMAC were added to aliquots of stirred slurry over a few seconds, followed by 30 seconds of stirring. Slurry samples were then passed through a 60-mesh stainless steel screen, and the filtrate was evaluated with the streaming current device. The condition of surface saturation was equated with the maximum added amount of polymer addition to the slurry that did not change the streaming current measurement of the filtrate from negative to either zero or a positive value.

Supplementary Tests of the Fiber Slurry

The pH and conductivity were measured after addition of chemical additives to 0.6% consistency slurry samples. Electrophoretic mobilities of fine particles were obtained from filtrate samples, using a Lazer-Zee® instrument from PenKem. Fiber length distributions and other related information were determined with the Fiber Quality Analyzer (FQA) from Optest Equipment Inc. Approximately 1500 fibers were evaluated in each test, at a rate of approximately 7 fibers per second. Freeness tests were carried out according to TAPPI Method T227. Water retention values were determined according to TAPPI Useful Method UM 256.

Paper Handsheets

Handsheets for baseline tests, with no chemicals, were prepared according to TAPPI method T205, except that the fiber amount doubled, yielding approximately 120 g/m^2 basis weight. Oven-drying was for 8 minutes at 105 ^{o}C,

providing a final moisture of about 5%. The paper was then equilibrated under TAPPI standard conditions.

Groups of ten replicate handsheets were prepared as follows, representing different levels of poly-DADMAC addition. Moist pulp corresponding to 24 g oven-dry mass was diluted to 4000 ml with tap water. Selected amounts of 0.4% poly-DADMAC were added and mixed for 2 minutes. Then, except in the case of the blank, an amount of 0.5% solids CMC solution corresponding to 2% mass on oven-dry fiber mass was added. The whole mixture was agitated gently for an additional 10 minutes. Handsheets were prepared as before.

After equilibration at TAPPI standard temperature and humidity, each group of handsheets was weighed. The five handsheets closest to each other were selected for further testing, and the remaining five were stored separately in plastic bags. Light scattering coefficients were determined as in TAPPI Method T425 om-86. Compression strengths (STFI method) were determined according to TAPPI Method T826. Tensile strength and breaking length were determined according to TAPPI Method T494.

To evaluate strength and other attributes of recycled fibers, the scraps and extra handsheets from the first cycle were used for a new set of nine secondary paper sheets. The pulp was soaks for four hours, followed by five minutes in a TAPPI disintegrator (TAPPI Method T05). The slurry was used, without further chemical addition, to form recycled handsheets, following the same procedures as before. Excess slurry was used to evaluate freeness, fiber length distribution (FQA tests), water retention, and electrical conductivity.

RESULTS AND DISCUSSION

Baseline Tests

Table 1 shows how drying and reslurrying of unbleached kraft pulp affected fiber properties in the wet state, in the absence of chemicals. The initial freeness of this refined, never-dried pulp was 426 ml CSF. The conductivity was 365 μS/cm. As shown, the water retention value (WRV) fell by about 24% due to drying and resuspension, irrespective of the drying temperature. This change, as noted earlier [6,59], is attributed to closure of pores in the cell wall [7-14]. The fines content was increased moderately, consistent with a moderate refining effect of the TAPPI disintegrator [60]. The results showed little change in fiber length.

Table 2 compares properties of paper formed from never-dried and once-dried fibers in the absence of polymers. In agreement with previous work [7-14], drying and recycling of the kraft fibers decreased paper strength. Compression strength fell by approximately 16-21%, and the tensile breaking length fell by approximately 11-23%, when comparing the recycled handsheets to the initial

handsheets. Zero-span tensile strength was not adversely affected by recycling; therefore, the observed strength loss cannot be attributed to loss of individual fiber strength [33]. The lower apparent density of the recycled sheets, under constant conditions of handsheet preparation, is consistent with a lower conformability of the fibers to each other, which helps to explain the lower strength. The light scattering coefficient increased due to recycling, which provides further evidence that there was less relative bonded area in the recycled handsheets [33,61].

Results of tests with drying at room temperature *versus* oven-drying were similar to each other. The 95% confidence limits of the strength results for the dried handsheets overlap each other, regardless of the drying temperature. These findings justified carrying out the remaining tests with air drying, under TAPPI standard conditions. Also, the TAPPI conditions were judged to be more precisely reproducible compared to the oven-drying.

Adsorption of Poly-DADMAC

As shown in Fig. 3, approximately 54 μeq of poly-DADMAC was sufficient to saturate the adsorption capacity of one gram of fibers, oven-dry basis, under the defined conditions (see Experimental). The saturated condition corresponded to 0.87% of poly-DADMAC based on oven-dry fiber mass.

Results of micro-electrophoresis tests, shown in Fig. 4, indicate that the fiber fines surfaces already had positive zeta potentials after exposure to poly-DADMAC at well below the saturation level. This means that the point of zero zeta potential might be represented by case "A" in Fig. 1, a condition where the surface of the fibers is partly covered with cationic polymer.

Results of fiber-pad streaming potential tests, shown in Fig. 5, indicate that the fiber surfaces became neutral at an addition level of about 25 μeq/g poly-DADMAC, about twice the level that was indicated by the micro-electrophoretic tests of fiber fines under the same conditions of treatment. These results are consistent with earlier findings [62]. The difference is consistent with the highly porous nature of fibers. The small fiber fines evaluated by microelectrophoresis apparently become saturated with polyelectrolyte sooner than the fibers, when both are treated together in the same mixture. Continued diffusion of polyelectrolytes into the cell walls of the fibers, which are mainly sensed during the streaming potential tests, means that the outer fiber surfaces have a lower density of cationic polymer, compared to the fines, at any stage during a titration.

Water Retention and Freeness *vs.* Polymer Addition

Figure 6 shows water retention values (WRVs) of pulp that was reslurried after being treated sequentially with poly-DADMAC at various levels, followed by carboxymethylcellulose (CMC) at 2% on oven-dry fiber mass, and then formed

into handsheets, which were dried at room temperature. There was a weak maximum in WRV at intermediate poly-DADMAC addition before the anionic polymer.

Though the WRV test is most often used to evaluate changes in the water-holding capacity of fiber cell walls, one also can expect a contribution from water imbibed within adsorbed polymers. If one assumes that the amount of adsorbed CMC is proportional to the increase in WRV relative to the blank, then the results are consistent with the illustrations shown in Fig. 2. In particular, it is reasonable to expect a fall-off of CMC adsorption if excess poly-DADMAC in solution forms neutral polyelectrolyte complexes with the CMC and those complexes fail to adsorb onto the fiber surfaces.

The preceding interpretation of water retention data was supported by freeness test results. At poly-DADMAC levels corresponding to the saturation level and higher, the net effect of dual-polymer addition was to increase the freeness. Freeness increased with increasing poly-DADMAC pretreatment, up to an optimum level, and then fell again at the highest level tested. Previous studies have shown similar optima, also apparently controlled by surface charge phenomena, in the case of pulp slurries treated with a single, highly cationic polymer [63-64]. If the changes in WRV merely indicated the refining degree, then one would expect an inverse correlation between WRV and CSF values. No such correlation was found.

Strength Effects of Polymer Addition

As shown in Fig. 7, treatment of never-dried fiber with poly-DADMAC followed by CMC had the potential to increase the compression strength of both the primary sheets and the sheets formed by recycling the same fibers without further chemical addition. In both cases the most promising results were achieved at a poly-DADMAC pretreatment level of 0.87%, *i.e.* at the level corresponding to fiber surface saturation, according to the streaming current tests discussed earlier.

Figure 8 shows a somewhat different trend in the case of tensile strength. Tensile breaking lengths of both the primary and recycled sheets increased with increasing poly-DADMAC treatment, ahead of the CMC. Unlike the compression tests, there was no distinct fall-off when the poly-DADMAC was raised above the level corresponding to fiber surface saturation.

The fact that results of compression tests and tensile tests showed different dependency on polymer treatment conditions is consistent with earlier findings [6]. Increased compression strength is favored by adhesive substances that are relatively rigid [34]. By contrast, a more flexible layer of adhesive material ought to be favorable for tensile strength, since such a condition might allow a better distribution of stress within the paper. Further work is needed to determine whether precipitation of polyelectrolyte complexes onto the fiber surfaces might

have played a role in these results, especially at the highest levels of poly-DADMAC treatment considered.

Apparent Density and Light Scattering

Table 3 shows additional test results. There was a weak maximum in apparent density corresponding to an intermediate dosage of poly-DADMAC pretreatment (1.73%) before the CMC addition, both for the primary handsheets and the recycled handsheets made from the same fibers without further chemical treatment.

The trends for light scattering coincided more closely to the compression strength data. The lowest light scattering of the recycled sheets corresponded to surface saturation with poly-DADMAC. A lower light scattering coefficient generally indicates fewer air-solid interfaces within the paper. One way to decrease such interfaces is to create more (optically) bonded area between fibers [33,61]. Further work will be needed to determine the extent to which such a mechanism plays a role in dry-strength treatments of this type.

CONCLUSIONS

1. The effectiveness of a dual-polymer dry-strength treatment of unbleached kraft pulp depended on the dosage of the first additive. The optimum level of poly-DADMAC pretreatment for compression strength was 54 μeq/g (0.87%) based on oven-dry fiber. The second additive was carboxymethylcellulose (CMC) at a constant addition level of 2%.

2. Conditions that most benefited the strength of the primary sheets also had the best effect on the strength of recycled sheets.

3. The proposed fiber surface saturation model provides a rationale for maximizing the effectiveness of dual-polymer treatments for compression strength. Below the saturation level of the first additive (cationic), increasing amounts are expected to increase the net effectiveness of the dry-strength system. Above the saturation level, excess cationic polymer in solution is expected to complex with the second additive, leading to unpredictable effects.

4. Paper mill trials are recommended to validate the commercial use of dry-strength chemicals. Dry strength depends also on pulping operations, refining practices, and wet pressing, in addition to chemical additives. Also, the present study does not deal with effects of interfering substances.

ACKNOWLEDGEMENTS

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TABLES

Table 1. Pulp Properties, Never-Dried vs. Recycled

Pulp condition:		Never-dried (1) *	Air-dried	Never-dried (2) *	Oven-dried
Test	Units				
Water retention value ^	% water / oven-dry fiber	244.2 ± 6.3	186.5 ± 5.4	238.1 ± 13.7	181.5 ± 1.21
Fines content	%	30.48	33.49	28.40	32.67
Fiber length ^	mm (> 0.2 mm)	1.81 ± 0.07	1.76 ± 0.06	1.77 ± 0.07	1.75 ± 0.06
* Tests carried out in parallel with air-drying tests ** Replicate tests performed in parallel with oven-drying tests ^ Ranges (±) indicate 95% confidence intervals.					

Table 2. Paper Properties, Primary vs. Recycled

Paper condition:		Primary	Recycled	Primary	Recycled
Drying, first cycle		25 ^{o}C	25 ^{o}C	105 ^{o}C	105 ^{o}C
Drying, second cycle		-	105 ^{o}C	-	105 ^{o}C
STFI compression *	Nm/g	32.2 ± 2.5	25.3 ± 1.9	29.8 ± 2.7	25.2 ± 1.7
Breaking length *	km	6.15 ± 0.42	5.47 ± 0.36	7.02 ± 0.47	5.38 ± 0.27
Zero-span tensile *	km	34.8 ± 1.2	36.4 ± 3.2	35.1 ± 3.0	39.3 ± 1.9
Apparent density	g/cm^3	0.77	0.69	0.76	0.68
Light scat. coef. *	m^2/kg	9.1 ± 1.2	10.4 ± 1.0	7.7 ± 1.0	10.5 ± 1.2
* Ranges (±) indicate 95% confidence intervals.					

Table 3. Paper Test Data, Primary Sheets

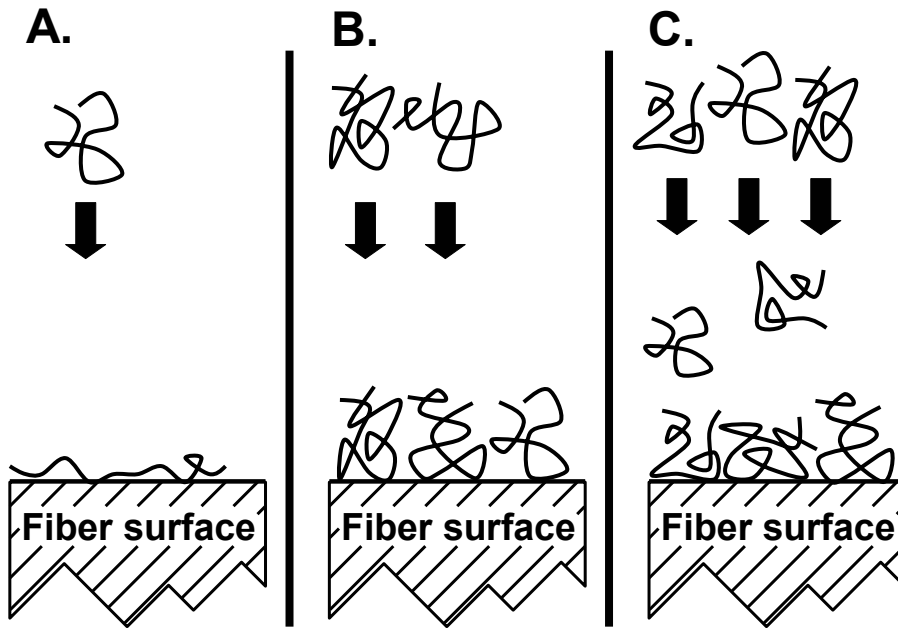| Poly-DAD-MAC (%)	CMC (%)	Apparent Density (g/cm^3)		Light Scattering Coefficient (m^2/kg)
		Primary	Recycled	Recycled
0.00	0	0.702	0.657	11.4 $\pm$ 1.9
0.00	2	0.714	0.654	11.9 $\pm$ 4.1
0.43	2	0.714	0.681	11.5 $\pm$ 1.0
0.87	2	0.717	0.663	10.3 $\pm$ 1.3
1.33	2	0.723	0.675	10.3 $\pm$ 1.7
1.73	2	0.756	0.699	11.0 $\pm$ 3.6
2.37	2	0.714	0.663	12.0 $\pm$ 1.3

FIGURE CAPTIONS

Fig. 1 – Idealized models for adsorption of polyelectrolyte onto an oppositely charged surface either (a) below, (b) at, or (c) above the saturation level
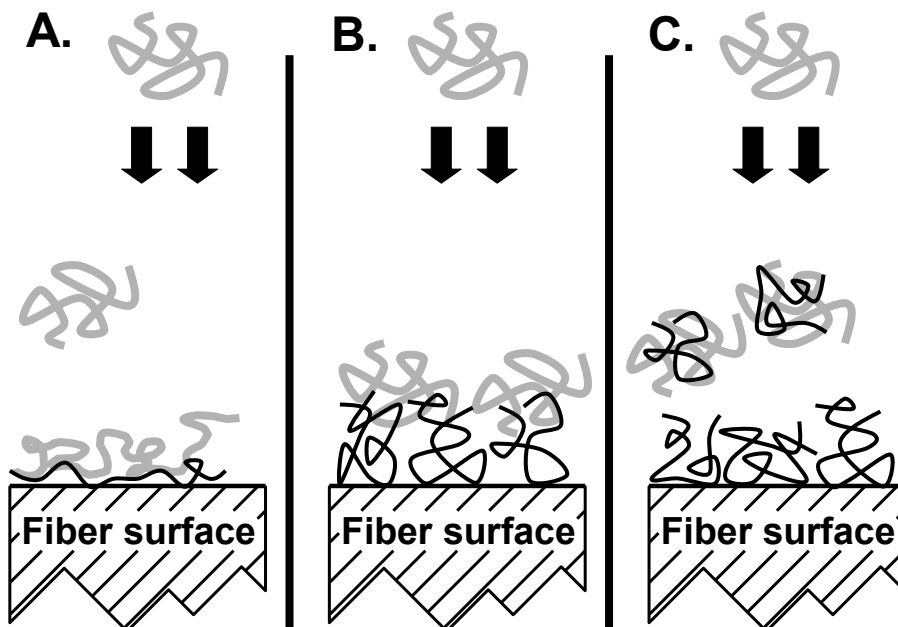
Fig. 2 – Idealized models for adsorption of an oppositely-charged polyelectrolyte either (a) below, (b) at, or (c) above the saturation level of the first polyelectrolyte
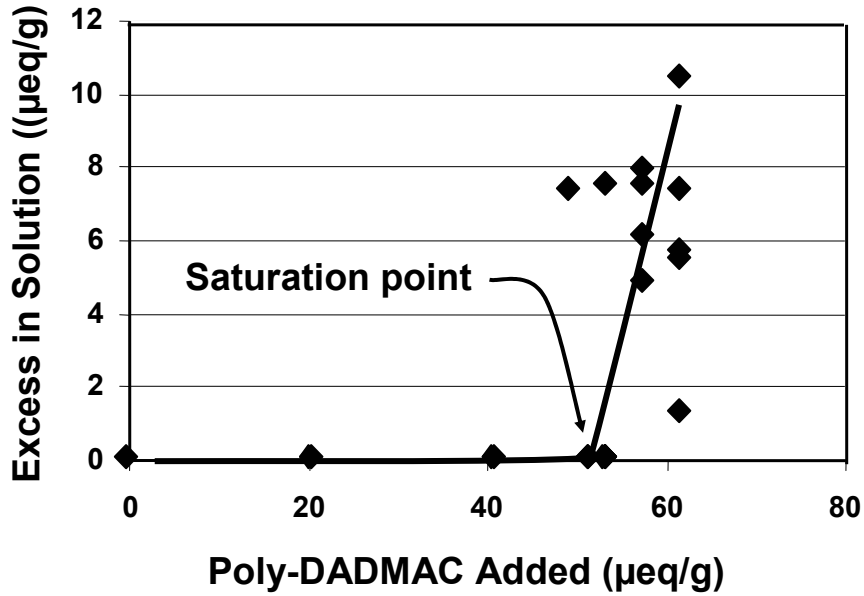
Fig. 3 – Determination of the saturation level of poly-DADMAC on unbleached kraft fibers by back-titration of the filtrate with PVSK to zero streaming current
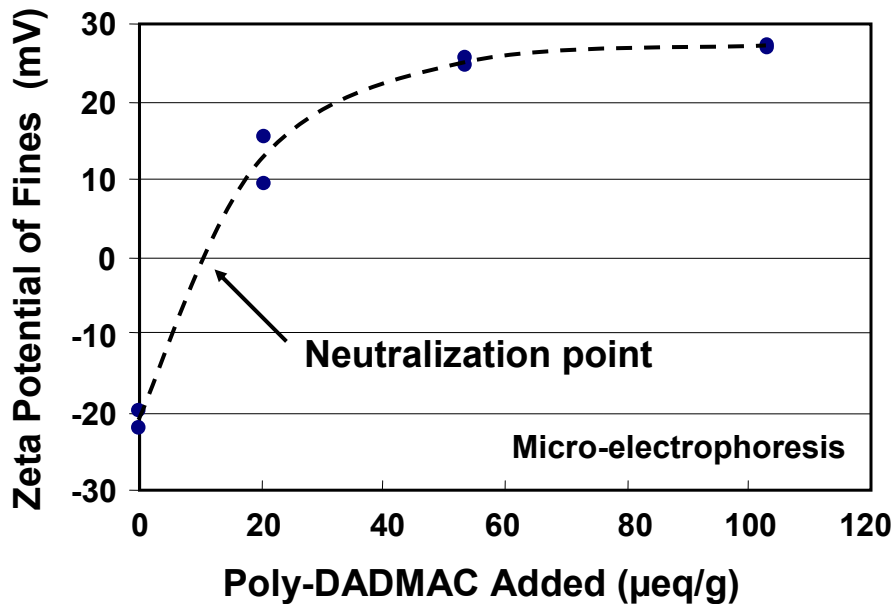
Fig. 4 – Zeta potential of fiber fines by microelectrophoresis, *versus* poly-DADMAC addition to unbleached kraft furnish

Fig. 5 – Zeta potential from fiber-pad streaming potential tests *versus* poly-DADMAC addition to unbleached kraft furnish

Fig. 6 – Water retention values (WRVs) of unbleached kraft pulp *versus* addition level of poly-DADMAC, prior to addition of 2% CMC, drying, and reslurrying. The blank (first bar) corresponds to no chemical addition.

Fig. 7 – STFI compression strength of primary and secondary handsheets *versus* the addition level of poly-DADMAC, followed by 2% CMC. Chemicals were added only to the never-dried pulp, not during recycling. The blank (first set of bars) corresponds to no chemical addition.

Fig. 8 – Tensile breaking length of primary and secondary handsheets *versus* the addition level of poly-DADMAC, followed by 2% CMC. See Fig. 7 for other notes.

FIGURES

A.   **B.**   **C.**

Fig. 1 – Idealized models for adsorption of polyelectrolyte onto an oppositely charged surface either (a) below, (b) at, or (c) above the saturation level

A.   **B.**   **C.**

Fig. 2 – Idealized models for adsorption of an oppositely-charged polyelectrolyte either (a) below, (b) at, or (c) above the saturation level of the first polyelectrolyte

Fig. 3 – Determination of the saturation level of poly-DADMAC on unbleached kraft fibers by back-titration of the filtrate with PVSK to zero streaming current

Fig. 4 – Zeta potential of fiber fines by microelectrophoresis, *versus* poly-DADMAC addition to unbleached kraft furnish
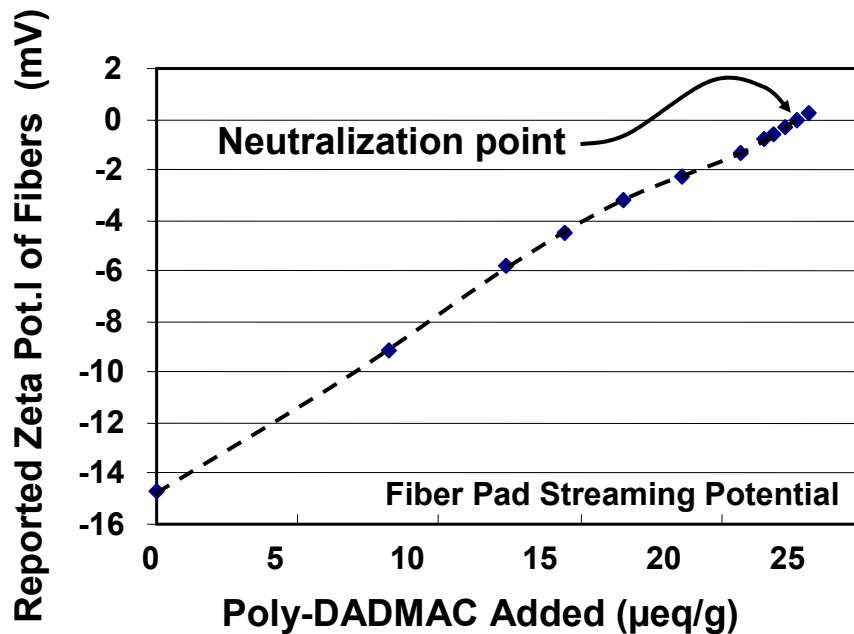
Fig. 5 – Zeta potential from fiber-pad streaming potential tests *versus* poly-DADMAC addition to unbleached kraft furnish
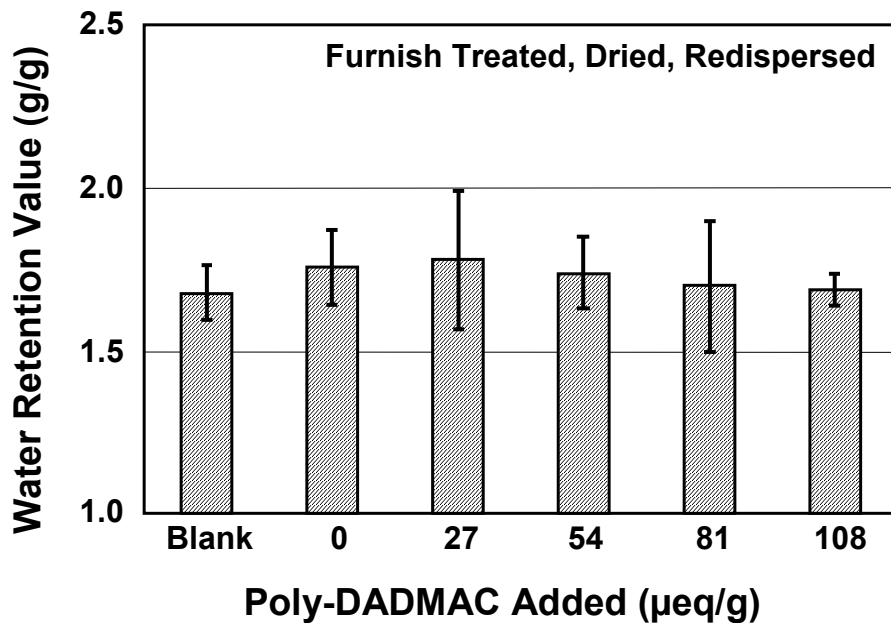

Fig. 6 – Water retention values (WRVs) of unbleached kraft pulp *versus* addition level of poly-DADMAC, prior to addition of 2% CMC, drying, and reslurrying. The blank (first bar) corresponds to no chemical addition.
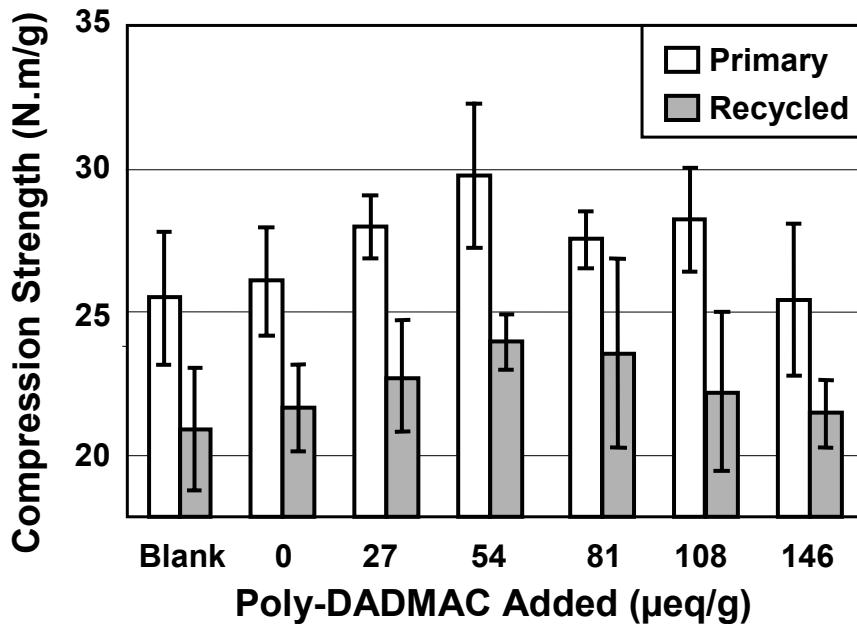
Fig. 7 – STFI compression strength of primary and secondary handsheets *versus* the addition level of poly-DADMAC, followed by 2% CMC. Chemicals were added only to the never-dried pulp, not during recycling. The blank (first set of bars) corresponds to no chemical addition.
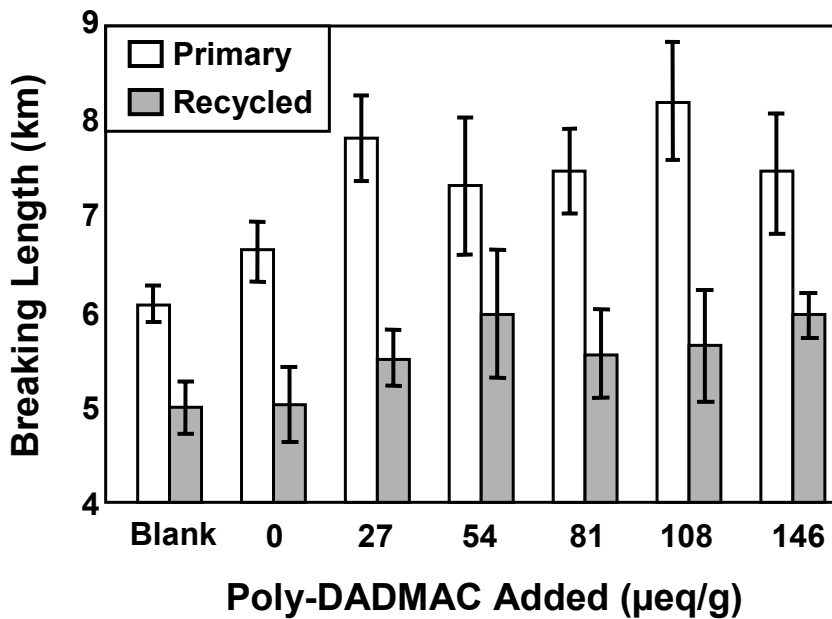

Fig. 8 – Tensile breaking length of primary and secondary handsheets *versus* the addition level of poly-DADMAC, followed by 2% CMC. See Fig. 7 for other notes.