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Charge and the Dry-Strength Performance of Polyampholytes. Part I: Handsheet Properties and Polymer Solution Viscosity

J. SONG, Y. WANG, M.A. HUBBE, O.J. ROJAS, N. SULIĆ, and T. SEZAKI

Paper strength was increased by adding random terpolymers having a fixed ratio of basic to acidic monomeric groups to bleached kraft fibre slurries over a wide range of pH. Subsequent treatment of the fibre slurries with polyaluminum chloride (PAC) increased tensile breaking length further. By contrast, PAC tended to reduce the dry-strength contribution of a cationic polyelectrolyte having the same mass and cationic monomer content as one of the polyampholytes. The reason for adding the PAC last to the mixture was to evaluate possible interactions of fresh, highly cationic aluminium species with the polymers as well as with the fibre surfaces. It is proposed that the observed effects are due to the influence of pH and ionic aluminum species on the molecular conformations, as well as to the electrokinetic behaviour of the solids exposed to the polyampholytes. Results of solution viscosity tests indicated more expanded polyampholyte conformations resulting from PAC addition, especially in those cases where dry strength advantages of PAC addition were observed.

Nous avons accru la résistance du papier en ajoutant des copolymères triples aléatoires ayant une proportion fixe des groupes monomères basiques et acides à des suspensions de fibres kraft blanchies sur une vaste échelle de pH. Le traitement subséquent de la suspension de fibres avec du polychlorure d'aluminium a accru encore davantage la longueur de rupture à la traction. Par contre, le polychlorure d'aluminium avait tendance à réduire la contribution à la traction à l'état sec d'un polyélectrolyte cationique ayant la même masse et la même teneur en monomère cationique que l'un des polyampholytes. L'ajout en dernier du polychlorure d'aluminium au mélange visait à évaluer les interactions possibles des espèces d'aluminium fraîches très cationiques avec les polymères et avec les surfaces des fibres. Nous proposons que les effets observés soient attribuables à l'influence du pH et des espèces d'aluminium ioniques sur les conformations moléculaires, ainsi qu'au comportement électrocinétique des solides exposés aux polyampholytes. Les résultats des essais de viscosité de la solution ont indiqué d'autres conformations après l'ajout de polychlorure d'aluminium, en particulier dans les cas où des avantages de résistance à l'état sec ont été observés après l'ajout de polychlorure d'aluminium.

INTRODUCTION

Recent work in our lab has confirmed earlier reports showing superior dry-strength and related effects resulting from the wet-end addition of soluble polymers having both positive and negative ionic groups [1–4], the so-called polyampholytes. The present work is intended to clarify the relationship between such strength gains and the charged nature of these polymers.

Any discussion of dry-strength effects of papermaking wet-end additives needs to begin with the consideration of bond formation between fibres [5]. Work by Howard and Jowsey [6] showed that the effects of cationic starch, the most widely used dry-strength additive, are consistent with increased joint strength per unit bonded area. McKenzie [7] and Pelton et al. [8] described dry-strength development in terms of a three-dimensional solubilization of the bonding agent with wood-derived macromolecules extending from fibre surfaces. The subject of joint strength and the role of bonding agents have been reviewed recently [9].

Based on recent work, interfibre bond strength is expected to increase with the increasing molecular mass of a dry-strength additive [10]. Evidence suggests that the initial adsorbed conformations are random coils, similar to the situation in the bulk solution, and that the macromolecules rearrange themselves subsequently onto the substrate surfaces [11,12]. Due to the relatively short processing times in the wet end of a paper machine, one cannot assume that adsorbed conformations reach an equilibrium state. The degree to which the polymer adopts a flattened adsorbed conformation, or otherwise rearranges itself, is expected.
to depend on time, molecular mass, the charge density of the polymer, the strength of interactions between molecular segments and the substrate, the degree of solubility of the polymer in the solution, the existence of branching or crosslinking within the polymer and the ionic strength of the solution [13–15]. The molecular extension of polyampholytes is expected to depend on the same factors, and also on the ratio of monomeric charged groups of each sign [16–19]. The adsorption of polyampholytes has also been considered by others [20,21]. Viscosity tests have been found to be a convenient way to study factors that affect molecular extension [16,22–24].

Soluble aluminum compounds have been of great interest to paper technologists [25], as well as to scientists investigating the ionic speciation [26,27] or optimization of aluminum compounds for coagulation of suspensions [28–31]. Complexation can be expected when aluminum compounds are added to solutions of anionic polyacrylates [25,32,33]. Recent results suggest that certain ionic species of aluminum can maximize interactions with anionic polyacrylates [34], as well as the coagulation of suspensions of negatively charged particles [31]. The present work is aimed at elucidating the effect of polyampholyte overall charge density and charge ratio on the development of dry strength and the synergies that occur in the presence of aluminum ions.

The experimental approach employed in the present work involved the treatment of bleached kraft fibre slurries with a series of acrylamide-based polyampholytes, all having similar molecular mass but with a wide range of charge densities. To achieve the efficient retention of the polymers onto the weakly negative fibre surfaces, the ratio of basic to acidic groups was 5:4. This ratio caused the polyampholytes to have a weak net positive charge under neutral to positive pH conditions. After the treatment of the polyampholytes, certain slurry samples were treated subsequently with polyaluminum chloride (PAC). The order of addition was selected to give the greatest opportunity for interaction of transient highly cationic aluminum ions [26,27] with carboxylate groups on both the polyampholytes and the fibre surfaces. Parallel tests were carried out with polyelectrolyte samples (single charge), making it possible to distinguish behaviours unique to polyampholytes.

### EXPERIMENTAL

Experiments were conducted in deionized water prepared with an ion-exchange system from Pureflow, Inc., Whittier, CA, USA. The PAC was Compozii Eka ATC 8210 from Eka Chemicals, Paper Chemicals Div., Marietta, GA, USA. The product was added on an as-received basis. Other inorganic chemicals all were reagent grade.

### POLYAMPHOLYTE PREPARATION AND CHARACTERIZATION

Polyampholyte and polyelectrolyte samples were prepared by free-radical polymerization, following the molar content of charged monomers indicated in Table I. The cationic monomer was N-[3-(N',N'-dimethylamino)methyl]acrylamide (DMAPAA), a tertiary amine. The anionic monomer was a dicarboxylic acid, itaconic acid (IA). In each case, a sufficient amount of neutral acrylamide monomer was added to adjust the total molar charge content to a fixed value and the molar ratio of cationic to anionic groups was also kept constant (5:4 for samples A–D). The molar % of DMAPAA and IA was corroborated by 1H and 13C nuclear magnetic resonance. Solution viscosities, as shown, were obtained with a Brookfield Model BBL viscometer (Tokimec, Inc., Tokyo, Japan) at ~15% solids at 25°C, with pH = 4, and with electrical conductivities as indicated in Table I.

### HANDSHEET PREPARATION

Tests involving handsheets were carried out with bleached hardwood kraft fibres that had been beaten with a laboratory Hollander refiner (Valley Machinery Co., Appleton, WI, USA) to a Canadian standard freeness (CSF) value (TAPPI T 227 [35]) of 440 mL. Then, the refined fibres were placed in a 200-mesh screen chamber of a Bauer-McNett classifier apparatus (see TAPPI Method T 233 [36]). The classifier was run for 15 min, per batch, to substantially remove fibre fines from the suspension, a process that is sometimes called decrilling. The decrilling procedure was carried out to simplify the interpretation of results to be presented below, since any polymer adsorbed onto fibres is retained in the final paper. The decrilled suspension had a freeness of ~600 mL CSF.

Then, the fibres were resuspended as a 0.5% slurry in 10−4 mol/L sodium bicarbonate solution, to which sufficient sodium sulphate had been added to reach an electrical conductivity of 1000 μS/cm at 23°C. Polyampholyte solutions were added at selected levels, as will be noted below, and with constant stirring to the fibre suspension. Stirring was continued 60 s before the preparation of handsheets. To maintain the same salt concentration during the formation of the paper, sufficient sodium sulphate solution to achieve an electrical conductivity of 1000 μS/cm was added to the British sheet mold just before the fibre slurry was added to make the handsheets, following TAPPI Method T 205 [37].

In the case of tests involving PAC addition, the pH was adjusted initially with NaOH or H2SO4. The polyelectrolyte or polyelectrolyte solution was added first, followed by PAC addition. The pH of the fibre slurry was prejudged in such a way that the suspension's pH reached the reported value upon addition of PAC. Sufficient sodium sulphate and either NaOH or H2SO4 were added to the handsheet mold so that the same pH and electrical conductivity were maintained throughout the forming process. The reason for adding the PAC last was to allow the immediate interaction of aluminum ions with carboxylate groups in the system, including those on the polymers. A different order of addition, in which PAC was added first to the suspension, though it would favor the interaction of the aluminum ions with fibre surfaces, also would allow a greater proportion of Al(OH)3 in suspension before the ions even have a chance to interact with the charged polymers that are the main focus of the present work.

### VISCOSITY TESTS

Viscosities of the 0.1% solids aqueous polymer solutions were measured with an Ubbelohde (Cannon Instrument Co., State College, PA, USA) viscometer in a thermostated water bath at 25.0°C with the addition of sufficient NaCl so that the resulting ionic strength at different pH values remained at 0.01 mol/L. The pH was adjusted with HCl or NaOH.

### RESULTS AND DISCUSSION

Figure 1 compares the tensile breaking length results for handsheets prepared at the
1% level of polymer treatment, as outlined further in Experimental. Results labelled as A through G correspond to the polymers employed (see Table I). As shown, treatment with the polyampholytes (samples A–D) resulted generally in strength gains that were far superior to those achieved by the simple polyelectrolytes (samples F and G).

Results shown in Fig. 1 raise various questions involving the effects of electrical charges. For example, in the absence of PAC, why was the highest strength achieved at an intermediate charge density of the polyampholyte, sample C, which had a molar content of 10% tertiary amine groups and 8% carboxyl groups? And why was the highest strength achieved when a small amount of the highly cationic aluminum-based additive PAC was added to the polyampholyte sample having the lowest density of ionizable groups (sample A)?

Further questions related to the way polyampholytes function as dry-strength agents arise from the results of tests at various pH values, as shown in Fig. 2. Comparing the results obtained at pH 4 (Fig. 2A) versus pH 8.5 (Fig. 2B), it is apparent that the PAC addition promoted the dry-strengthening effect with all of the polyampholytes at the higher pH of 8.5, but such treatment with PAC had less strength benefit at pH = 4. Also, it is worth questioning why the dry-strength performance of the cationic polyelectrolyte F was reduced by PAC addition.

Taken individually, most of the effects of PAC treatment on breaking length, in cases where the fibres had been treated with polyampholytes, were not statistically significant at the 90% confidence levels. What is notable is that PAC treatment, especially at the intermediate level of 0.2% on fibre solids, increased the mean value of breaking length in a large majority of cases. A possible explanation, to be considered in follow-up work, involves an expected complexation reaction of aluminum ions with one or more carboxyl groups. Complexation involving multivalent aluminum ions and carboxylate ions on the fibre surfaces would provide a likely anchoring site for interaction with the carboxylate groups on polyampholytes, increasing the efficiency of adsorption. Likewise, one aluminum ion, especially if it is of the oligomeric type mentioned above [26,27], might serve to crosslink carboxylate groups on two adjacent polyampholyte molecules. The combined effects may explain the enhanced efficiency with which polyampholytes contributed to interfibre bonding following treatment with PAC.

Another explanation, to be considered in follow-up work, involves the effects of PAC on charge characteristics of the polyampholytes and the fibre surfaces. Interaction of an aluminum with either an individual carboxylate ions or perhaps with a pair of such ions, in the case of a dissociated itaconic acid unit in the polyampholytes, would be expected to make the polyampholyte less negative or more positive in net charge. These issues will be dealt with in a companion article.

**Viscosity Analysis**

To account for the tensile strength results presented above, a series of experiments was carried out to evaluate the bulk properties of the polymer solutions. As shown in Fig. 3A, the relative viscosity of each of the polymer solutions was affected strongly by pH in the absence of salt. First considering the polyampholytes, samples A–D, there was a broad minimum in relative viscosity centered at ~6 < pH < 7. The viscosity of the polyampholytes increased generally with increasing difference in pH relative to neutrality, except that the viscosity fell again at the extremes of pH, below pH ~3 and above pH ~11. The ini-

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**Fig. 1.** Tensile test resulting from treatment of a slurry (pH 5) of bleached hardwood kraft at the levels of PAC as shown following treatment with polymer samples (see Table I) at the 1% level. The limit bars in Figs. 1–3 show 90% confidence intervals. Dashed outlines indicate simple polyelectrolytes.

**Fig. 2.** Results of tests similar to those in Fig. 1, except that the final pH of the slurry before sheet forming was (A) pH 4.0; (B) pH 8.5.
The reactivity ratios for pairs of monomers involved in our system were calculated according to the equations presented above and are shown in Table II.

While admitting the approximate nature of these estimated reactivities (the Alfrey-Price parameters available for the three monomers considered in this work do not take into account steric effects or ionic interactions), one can conclude that both of the ionic monomer groups (DMAPAA and IA) will tend to be consumed earlier by free-radical polymerization compared to the consumption of uncharged acrylamide monomers. In addition, it is reasonable based on the values in Table II to expect a higher frequency of reactions between base monomer groups relative to purely random polymerization. Such considerations imply a greater contribution of associations between net-negative segments and net-positive segments, both for intramolecular and intermolecular interactions [42].

Results corresponding to the polyelectrolyte samples F and G in Fig. 3 can be accounted for in a similar manner. Separate pH titrations showed that the cationic polyelectrolyte F had a pKₐ value of 9.8, and that the anionic polyelectrolyte G had pKₐ values of 4.1 and 6.8 for the two adjacent carboxyl groups [43]. Thus, one would expect the molecules in sample F to have a relatively expanded conformation at relatively low pH values corresponding to the charged, protonated form of the tertiary amine groups. Then, with increasing pH above a value of 8, it is reasonable to expect a drop in viscosity, consistent with a reduced molecular extension. Considerations in the case of the anionic polymer G are similar, except that decreasing the pH is expected to increase the proportion of protonated, uncharged
carboxylic acid groups relative to charged carboxylate groups on the polymer.

Results shown in Fig. 3B, corresponding to an electrical conductivity of 1000 $\mu$S/cm, show generally lower values of relative viscosity, consistent with the screening of electrical charge interactions within the macromolecular chain. However, the general pattern of the results was similar to that observed in the absence of salt. One effect that becomes more evident in Fig. 3B is the differentiation between the results for sample A, the lowest charge polyampholyte, versus those for samples with higher density ionic groups. Near neutral pH, the solution of sample A was considerably more viscous than the other polyampholyte samples. This observation suggests that the macromolecules in sample A do not have a sufficient density of oppositely charged ionic groups to contract the molecules to the same extent as the other polyampholyte solutions at pH = 7.

As shown in Fig. 4A, the addition of a low level of PAC (0.01% in solution, on an as-received basis) consistently increased the relative viscosities of polyampholyte solutions in the absence of added salt, both at pH = 4 and pH = 5. The opposite was seen in the case of simple polyelectrolytes, for which increasing PAC monotonically decreased relative viscosity. A higher level of PAC (0.1%) was no longer effective in increasing the relative viscosity of the polyampholyte solutions.

Though there may be various interpretations to account for the results in Fig. 4, it is apparent first of all that there exists a specific interaction between PAC and the polyampholytes. It is proposed that the increase in viscosity upon addition of PAC at the 0.01% level is due to complexation between cationic aluminum ionic species and carboxylate groups on the polyampholytes. Since all of the results in Fig. 4 pertain to pH values below the isoelectric points of the polyampholytes, such complexation would be expected to increase the net positive charge in each case, resulting in a more extended conformation. The reversion of the trend at higher PAC is again consistent with increasing ionic strength of the solution.

As indicated by the present results, the conformation of polyampholytes in bulk solution, in the presence and in the absence of PAC, is a key factor to explain the adsorption on fibres and the development in dry strength. This is logical if one considers that the behaviour of the macromolecules in the bulk solution has an important impact on the adsorbed state. For example, when the polymer is in a more contracted state in solution (lower viscosities) or in cases of lower solvency, the adsorbed amount on fibre surfaces is expected to increase and better bonding is expected as a result.

Support for the explanation above is found in our attempt to answer the first question that was proposed in relation to Fig. 1. At pH 5, sample C, used in the absence of PAC, produced the highest strength. Results for polyampholytes A and B are comparable, especially in the conditions used in Fig. 2A for breaking length measured for slurries prepared at pH 4. Nevertheless, it is shown consistently that, at pHs 4 and 5, the purely cationic polyelectrolyte (sample F) performed more poorly than the polyampholyte counterparts. The explanation for this observation lies in the facts that, at lower pH, the polyampholyte molecules have a smaller hydrodynamic radius (lower viscosity), which allows a more effective diffusion and adsorption on the adsorption sites, and they have a net positive charge that favours electrostatic interactions with the substrate (better adsorption). This explanation is also supported by the direct measurement of the amount of polymer adsorbed onto model cellulose films via quartz crystal microbalance (QCM) (data not shown). In fact, sample C showed the highest adsorbed amount at pH 4.

Polyelectrolyte F, which is purely cationic, showed a more extended conformation at pHs 4 and 5 due to intrachain repulsion (see viscosity data in Fig. 4B) and therefore is not expected to adsorb as effectively as polyampholyte B, C or D. This was confirmed also by measurements of the adsorbed amount on cellulose via QCM. In this condition, polyelectrolyte F produced relatively small improvement in fibre bonding.

Our results also point to the fact that, at low pH, the polyampholytes of intermediate cationic charge worked better than the other ones. In fact, electrostatic bridging between the polymer-coated surfaces, which is an important contribution to the development of paper strength, also reaches a maximum value at an intermediate value of charge density [44]. In the present case, this optimum situation occurred for sample C.

At high pH (pH 8.5), the addition of polyg G produced paper sheets of low breaking length. This is explained easily by the fact that, in this condition, the polyelectrolyte is effectively anionic and therefore electrostatic repulsion with cellulose surface charges prevents adsorption. Note that, for the formation of paper below the pKa of polyelectrolyte G (suspensions of pH 4 or 5), the breaking length of the sheet was higher than at pH 8. This is as expected since, at low pH, the negative charge is suppressed (less dissociation) and the polymer is able to adsorb. In the absence of electrostatic repulsion, entropic effects often favour the adsorption of high-molecular-mass substances from solution.

At pH 4 or 5, it is interesting to note the synergetic effect that occurs upon the addition of the highly cationic PAC additive to the
polymolybdate solutions (A–D). This effect is augmented in the case of polymolybdates of low overall charge density, when the pH is low, while it seems that, at a higher pH (8.5), this synergy occurs more markedly for polymolybdates of higher charge density. The reason for these effects is not obvious, since PAC and the polymolybdates bear the same sign of net charges. This is evident in the case of purely cationic polyelectrolyte F that produced paper with low breaking length. A plausible phenomenon that could explain the above effects is that PAC interacts with the carbohydrate moieties of the polymolybdate chains, rendering a net higher cationic character to the polymer that facilitates adsorption. Experimental evidence supports the observed effects [45,46]. On the other hand, the application of PAC with the anionic polyelectrolyte showed the lowest results, due to the fact that complexation and charge compensation occurs between the anionic polyelectrolyte and PAC and the effective charge of PAC is reduced.

CONCLUSIONS

– Charge effects, pH and the addition of PAC significantly affected the dry strength resulting from the treatment of bleached kraft fibres with polymers that contained both positively and negatively charged ionic groups. These polymolybdates yielded higher increases in dry strength compared to polyelectrolytes having ionic groups with a charge of only one sign. PAC addition generally benefited paper strength in cases where the fibre slurry had been treated with polymolybdates, but the opposite was true if the fibres had been treated with either a cationic or an anionic polyelectrolyte.

– Results of viscosity tests suggested that multivalent positive ions of aluminum form complexes with the carboxylate groups of polymolybdates, making them more cationic, and thus more expanded in solution.

– Significant effects of PAC on both viscosity and on strength development are consistent also with a crosslinking effect, in which aluminum ions may serve as bridges between carboxylate groups on different entities, such as two polymolybdate molecules or one such molecule and a fibre surface.

– Although it was generally the case that dry strength increases were maximized under pH conditions not far from those where the solution viscosities of polymolybdates were minimized, the optimum dry strength resulted from a combination of various effects, most importantly a minimum molecular extension and an optimization of electrical charge interactions.

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