# PAPER STRENGTH DEVELOPMENT AND RECYCLABILITY WITH POLYAMIDEAMINE-EPICHLOROHYDRIN (PAE)

Jielong Su,[a] Wade K. J. Mosse,[a] Scot Sharman,[a] Warren Batchelor,[a] and Gil Garnier [a,]*

The tensile strength behavior and recyclability of the paper prepared with the addition of polyamideamine-epichlorohydrin (PAE) were investigated. The dry and wet tensile strengths obtained with different PAE dosage were measured. The highest wet-to-dry strength ratio of 35% was obtained at 10 mg/g; above this addition level wet strength dropped slightly and then remained constant. The repulpability of strengthened paper was correlated directly with wet strength. The effect of electrolyte on tensile strength was also quantified by varying sodium chloride and calcium chloride concentration in the furnish stock. Without PAE, high salt concentrations (100 mM) reduced the tensile strength by 15-20%. At constant PAE addition level of 10 mg/g, low levels of salt addition (of either 10 mM NaCl or 10 mM $CaCl_2$) slightly improved the strength; paper strength decreased at high salts concentrations. The cation valency and concentration in the process water were important variables which affected the efficiency of PAE. These results present the significance of developing sustainable wet strength agents that can be applied in demanding salty conditions while maintaining the product recyclability.

*Keywords: Strength; Repulpability; Polyamideamine-epichlorohydrin (PAE); Recyclability; Paper; Wet-strength*

*Contact information: a: BioPRIA, Australian Pulp and Paper Institute, Department of Chemical Engineering, Monash University, Wellington Road, Clayton, VIC 3800, Australia.*
** Corresponding author: gil.garnier@monash.edu*

## INTRODUCTION

Strength distribution across paper is ensured by the multiple fibre-fibre bonds and controlled by the bonding area, the adhesion strength, and the fibre strength and size distribution. The Page equation describes the tensile failure of paper in terms of some of these critical variables (Page 1969). The strength of dry and wet paper is crucial to many applications, especially in packaging and tissue products. It has long been established that the tensile strength of paper is directly affected by the swelling behavior of the fibres interacting with water (Rowland Stanley 1977). The strength is controlled by fibre-to-fibre interactions that are developed during the process of paper formation, consolidation, and drying. In dry paper, hydrogen bonding is the dominant adhesive force and only acts over very short distances. As the bonds are water sensitive, the penetration of water into the dry paper matrix leads to a rapid weakening of fibre-to-fibre bonding and a concurrent loss in paper strength (Gardner et al. 2008). To lessen the reduction of paper strength upon contact with water, reactive water-soluble polymers such as polyamideamine-epichlorohydrin (PAE) are commonly used to improve the bonding between fibres, which constitutes the weak link in wet paper (Davison 1972).

The generally accepted mechanism of wet-strength development by PAE in paper is through the establishment of chemical bonds at fibre-fibre contacts. The process involves two steps: retention of the polymer and development of bonds. The main variables affecting PAE efficiency include its azetidinium concentration, the type of fibres, and the drying conditions (Obokata et al. 2002; Saito and Isogai 2005). Carboxyl groups, which significantly affect both PAE retention and reactivity, can be introduced to fibres by kraft pulping and through the bleaching process. When adding PAE to a slurry of cellulosic fibres, adsorption is driven by the electrostatic attraction between the anionic carboxylated groups on the fibre surface and the cationic azetidinium groups of the polymer (Espy and Rave 1988; Obokata and Isogai 2007). After PAE adhesion to cellulosic fibres, the curing process facilitates the formation of bonds between fibres. These bonds are covalent between the carboxyl groups of cellulose or hemicelluloses and the polymer's azetidinium group, resulting in inter-fibre bonds that are not water-soluble (Devore and Fischer 1993; Espy 1995). Therefore, special techniques such as a combination of mechanical energy and oxidizing agents are required for successful repulping (Chan 1994; Espy and Geist 1993).

While the fundamentals of PAE resin strength development mechanism are relatively well understood, the effects of PAE addition on recycling are more obscure. This is especially the case for optimizing water and fibre recycling for sustainability. The direct implications are the necessity to form paper with a furnish having very high salt concentration and the ability to fully and easily repulp PAE-made fibre products to insure full recycling. Indeed, many packaging grades are exclusively made of recycled fibres. In these circumstances, the addition of PAE is expected to fulfill two contradictory requirements. On one hand PAE is requested to provide permanent and strong fibre-fibre bonds; on the other hand, the resulting strengthened paper must remain fully recyclable. Very little quantitative information is available in this realm. It is the objective of this study to quantify the behavior of PAE from the modern perspective of sustainable papermaking.

The first part of this study quantifies the effect of PAE on paper strength development and repulpability. A new methodology was developed to quantify recycling. The second part investigated the effect of salt valency and concentration on paper strength with and without PAE. This study aims at quantifying the potential and limitations of reinforced strength agents in the context of sustainable papermaking.

## EXPERIMENTAL

### Materials

The commercial PAE (WSR 557 HP) was provided by Nuplex Industries (Australia) Pty Ltd (12.5% w/w solid content solution); PAE solutions were diluted with deionised water prior to each experiment. Analytical grade sodium chloride (NaCl) and calcium chloride ($CaCl_2$) were purchased from Sigma-Aldrich (Australia). Bleached eucalyptus kraft pulp was obtained from the dry lap sheet (NIST Standard reference material 8946).

## Methods

### *Handsheets preparation*

Cellulose handsheets were prepared according to the Australian/New Zealand Standard Method 203s. Basically, the dry pulp was thoroughly wetted by soaking in deionized water for about 12 hours. The pulp was transferred to a disintegrator (Model MKIIIC, Messmer Instruments Ltd), diluted to 2 L with deionized water, and disintergrated for 75,000 propeller revolutions. Prior to handsheet forming, the PAE solution was added to the pulp slurry in either salt-free or salt-containing conditions and stirred for 5 min. The pH of the pulp slurry mixture was non-adjusted, and the value was about 5. The addition quantity of PAE was based on oven dry grammage of 60 g/m$^2$. After manual couching and wet-pressing at 0.4 MPa for about 15 seconds, the sheets were cured in a drum-dryer at 100 °C for 10 min, in order to activate the bonds between the PAE and the cellulose surface.

### *Formation test*

The handsheet uniformity was measured with the Paper Perfect Formation Tester (Op Test Equipment Inc, Canada). The tester classifies formation quality in 10 formation components over a specific range and produces the formation value. The relative formation value (RFV) of each component relates to selected reference sheet (without PAE). RFV values less than 1 means that the formation quality of the tested paper is worse than the formation quality of the reference paper.

### *Tensile strength test*

The sheets were equilibrated at 23°C and 50% relative humidity for at least 24 hours before wet and dry tensile testing based on the Australian/New Zealand Standard Methods 448s and 437s. The test strip was slightly bent and the middle part touched to the surface of the deionised water for 2 seconds. The wetted length is about 25 mm. The width of sample strips was 15 mm and test span was 100 mm. An Instron tensile tester (Instron 5566) was used to record maximum tensile force with constant rate of elongation at 10 mm/min. The tensile index for each sample was calculated as tensile strength (expressed in newtons per metre) divided by basis weight (grams per square meter). The mean value was obtained from seven valid tests and the error bars in figures indicated the 95% confidence interval. T-Test was used to determine statistical significance of data.

### *Evaluation of recyclability of strengthened sheets*

The laboratory disintegrator (Model MKIIIC, Messmer Instruments Ltd) was used for evaluating the recyclability of the sheets. A 1.2 g handsheet was torn into small pieces of about 1 cm$^2$, added to 2 L deionised water, and disintegrated immediately for 3000 revolutions at room temperature (operation time of 1 minute). After repulping, the slurry from the disintegrated handsheet was screened in a fibre classifier (Brecht & Holl type, model BH-6/12) for 20 min through a 0.2 mm slot screen at a water flow rate of 2.5 L/minute. The rejects (fraction that did not pass the screen) were collected, dried at 105

°C for 4 hours and weighed. Repulping and classification were performed at ambient temperature in triplicate and the average was reported.

The repulpability index (R.I.) was defined as:

$$\text{R.I.} = \frac{\text{mass of dry sheet} - \text{mass of dry rejects}}{\text{mass of dry sheet}} \times 100 \qquad (1)$$

The index represents the percentage of fibres satisfactorily repulped and recovered. A higher value of R.I. indicates easier recycling process of the sheet.

## RESULTS AND DISCUSSION

### Effect of PAE Concentration on Paper Strength

Paper without PAE retained less than 10% of its original strength (dry) when wetted. Figure 1 shows that wet over dry strength ratio increased significantly to 28% at a PAE concentration of 5 mg/g (mg PAE per g oven dry cellulose fibre), to reach a maximum ratio of 33% at 10 mg/g. The ratio leveled off thereafter, at least to a PAE concentration up to 50 mg/g.

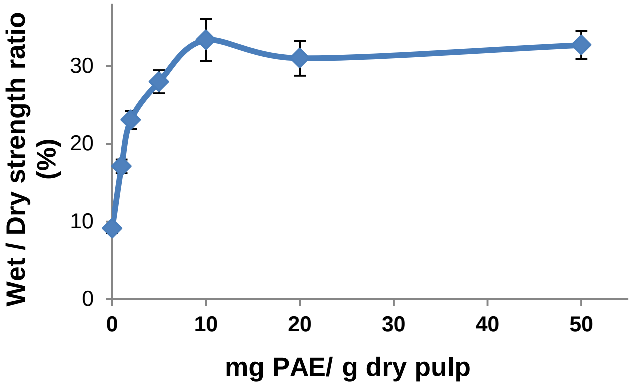

**Figure 1.** Effect of PAE dosage on the wet and dry strength ratio

The paper wet and dry tensile index both changed non-linearly with the addition of PAE (Fig. 2). At low PAE dosages, the fibre's surface was unsaturated and all polymer adsorbed onto the fibres. Paper strength increased with polymer addition in this regime. The wet tensile index (W.T.I.) increased with PAE addition up to 10 mg/g, to reach a maximum of 4.6±0.1 Nm/g; this was about four times the strength of the reference sheet. The W.T.I. reduced to 4.2±0.1 Nm/g at a PAE dosage of 20 mg/g and leveled off until 50 mg/g. The wet strength improvement is attributed to co-crosslinking with ester bonds forming between pulp carboxyl groups and PAE azetidnium groups. The decrease in paper strength at high PAE concentration could be attributed to homo-crosslinking of PAE, which was very sensitive to water and is weaker than the co-crosslinking involving PAE and fibres (Bates 1969; Espy and Rave 1988).

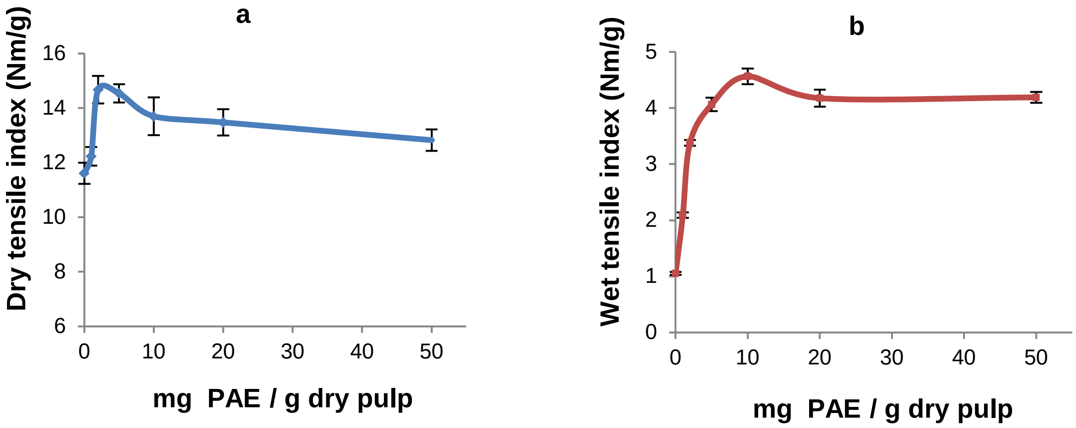

**Figure 2.** Effect of PAE concentration on the dry tensile index (a) and wet tensile index (b) of papersheets

In contrast to wet strength, the maximum dry tensile index of 14.7±0.5 Nm/g was achieved at 2 mg/g; at higher dosages there was a gradual decline in dry tensile index. Paper formation worsened upon PAE addition, especially at larger inspection sizes (Fig. 3). This was probably related to the high cationic charge and the medium molecular weight of PAE, promoting strong fibre flocculation. Therefore PAE has two antagonistic effects on paper strength. The first is a beneficial increase in fibre-fibre bond strength promoted by covalent bonds; the second is a detrimental effect of impaired formation caused by increased fibre flocculation. At low doses of PAE, the covalent bonding properties of the additive were dominant, and paper strength improved. As polymer addition increased further, fibre flocculation induced by PAE becomes significant and counteracted the strength improvement.

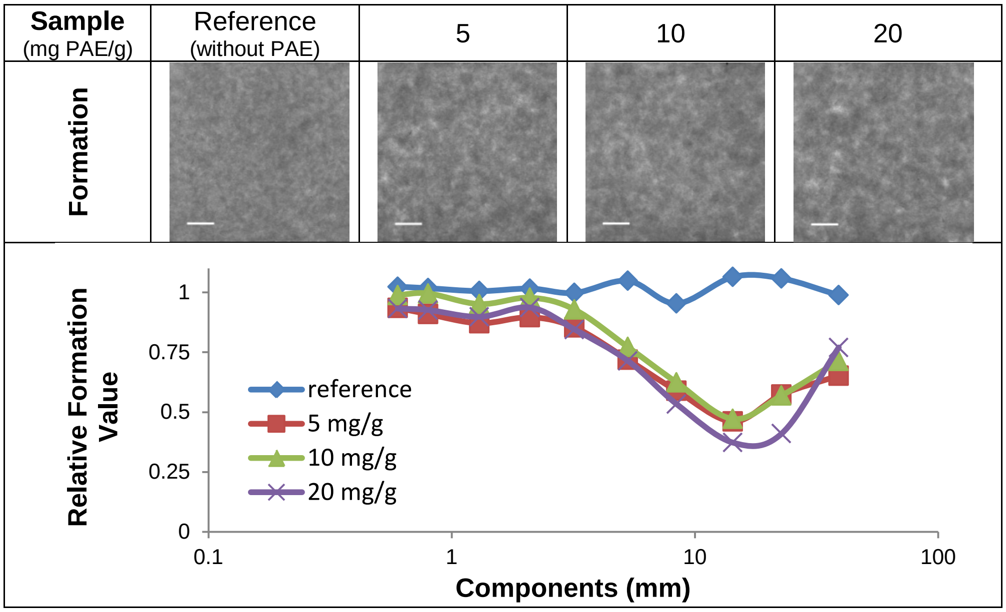

**Figure 3.** Formation of paper sheets with different PAE dosage (scale bar equals 1 centimeter).

## Recyclability of PAE Strengthened Paper

As there is no widely accepted standard test method to evaluate the recyclability of paper; each organization is left to define its own method. Repulping is the process in which paper is recycled into fibres capable of being used again in papermaking. This is achieved by subjecting a paper slurry to mechanical forces; chemical and bleaching aids are sometimes also used. In this study, a method initially developed by a paper company was modified to rate the sheet recyclability under constant operating parameters.

The effect of PAE concentration on repulpability is shown in Fig. 4. The paper's repulpability decreased in a non-linear fashion with increasing PAE concentration. A repulpability index (R.I.) of 100% for the control sheet indicated that the original sheet was totally recyclable under the experimental conditions. When the control paper sheet was wetted in recycling conditions, the hydrogen bonds between fibres were rapidly disrupted by the competing water molecules, leading to much weaker inter-fibre bonding. Under these circumstances, the paper sheet was very easy to break down into individual fibres upon a short exposure to mechanical shear force.

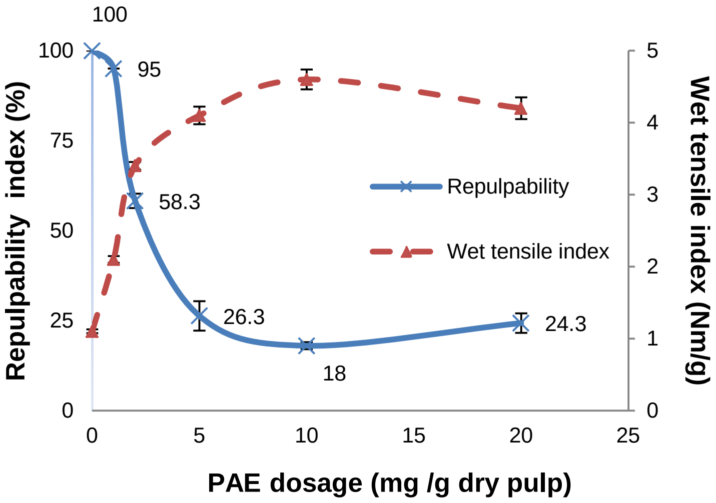

**Figure 4.** Effect on PAE concentration on repulpability index (solid line) and wet tensile index (dashed line)

Adding PAE increased inter-fibre bonding, thus inhibiting network breakdown and adversely affecting the recycling. The addition of 1 mg PAE /g fibre doubled the wet tensile index to 2.1 Nm/g, and the R.I. decreased to 95%, meaning that a small amount of rejects were left on the screen at end of processing. As the polymer dosage was increased to 2 mg PAE/g fibre, W.T.I. rose to 3.4 Nm/g and the R.I. value dropped sharply to 58%. By further increasing PAE dosage, the R.I. continued to decrease. The sheet was most difficult to repulp at a PAE dosage of 10 mg/g, the PAE concentration at which the greatest wet tensile index was observed. It was notable that paper sheets exhibited similar repulpability at PAE dosages of 5 mg/g and 20 mg/g, where the W.T.I. was very similar.

There was obviously a strong correlation between the paper wet-strength and its repulpability; this relationship was plotted in Fig. 5 in terms of W.T.I and R.I. The relationship was seen to be linear for the samples tested. The initial paper sample with no

PAE was excluded from the line, as there are no covalent bonds formed. No paper repulpability was extrapolated to occur at wet strength higher than 5 Nm/g, using the current method. The slope of the line was expected to vary as a function of the ratio of bond strength/mechanical shear; the wet-strength polymer chemical composition, the repulping configuration, and the power would be important variables. Bennington et al. (1998) applied a more mechanical analysis to the repulpability process. The proposed model described the repulping process at a pulp mass concentration no less than 1%, and concluded that the rate of defibrization depends on the amount of contact between the rotor and the suspension, the force imparted by the rotor, and the paper strength. In comparison with Bennington's work, the relationship curve from this study was achieved at a much lower fibre concentration (about 0.06%) and constant recycling time.

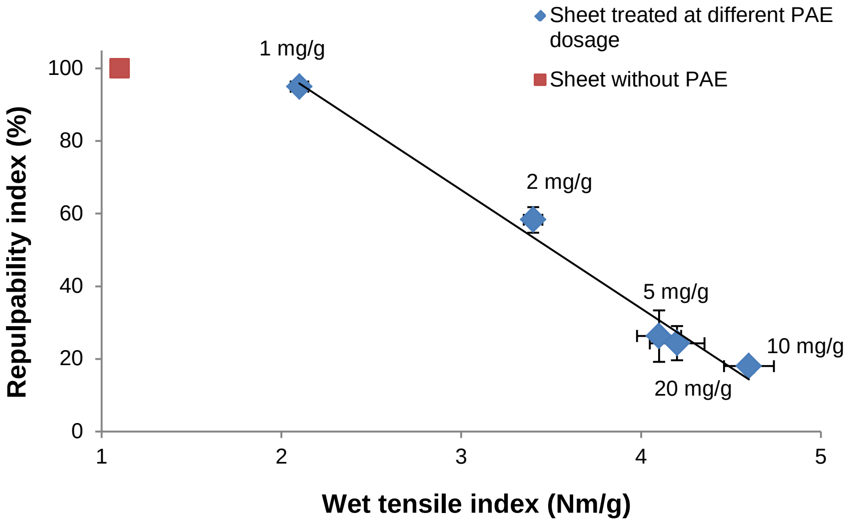

**Figure 5.** Plot of repulpability index versus wet tensile index obtained from sheets strengthened by PAE and a reference without PAE. Data in Fig. 4 were used to calculate the treadline.

## Effect of Electrolyte on Paper Strength

From the standpoint of paper physics, the formation and consolidation of paper structure may be altered by the presence of salt (Scallan 1979). Figure 6 presents the weakening of both dry and wet paper without PAE, which was observed when formed with high salt concentration (100mM of NaCl or $CaCl_2$) in pulp slurry. Dry tensile index declined from 10.7 Nm/g to 8.9 Nm/g with NaCl addition and to 9.1 Nm/g with $CaCl_2$ addition (Fig 6a). This can be attributed to three factors: reduced inter-fibre strength, reduced pore radius, and increased moisture content. The joint strength that holds fibres together is dependent on ionic strength. A decreased joint strength is expected as salt is added (Torgnysdotter and Wagberg 2004). Also the average pore radii of fibre was reported to decrease at high concentration (100 mM NaCl), and it was suggested that the smaller pores result in a lower molecular contact area between the fibres, reducing the joint strength (Andreasson et al. 2005; Forsstrom et al. 2005). Salts are known to affect paper hygroscopy. In this study, the moisture content of paper sheets upon equilibrium in a 50% RH environment was 5.5%, 6.3%, and 6.7% respectively for salt-free, NaCl, and $CaCl_2$ (100mM).

The wet tensile index of paper without PAE was reduced by 17% and 20% with NaCl and $CaCl_2$ respectively (Fig. 6b). The cellulose fibre surface can be regarded as a hydrogel when saturated in water. The decrease of salt-induced fibre swelling can be caused by an osmotic pressure differential resulting from a difference in concentration of mobile ions between the interior of the gel and the exterior solution (Grignon and Scallan 1980; Lindström 1992). A previous study presented evidence that fibre entanglements and friction are two important mechanisms controlling for the strength of wet paper (Tejado and van de Ven 2010). For this reason, the lower degree of swelling of fibres in saline environment may create a smaller friction area (Fig. 7), resulting in a paper web of lower wet strength.

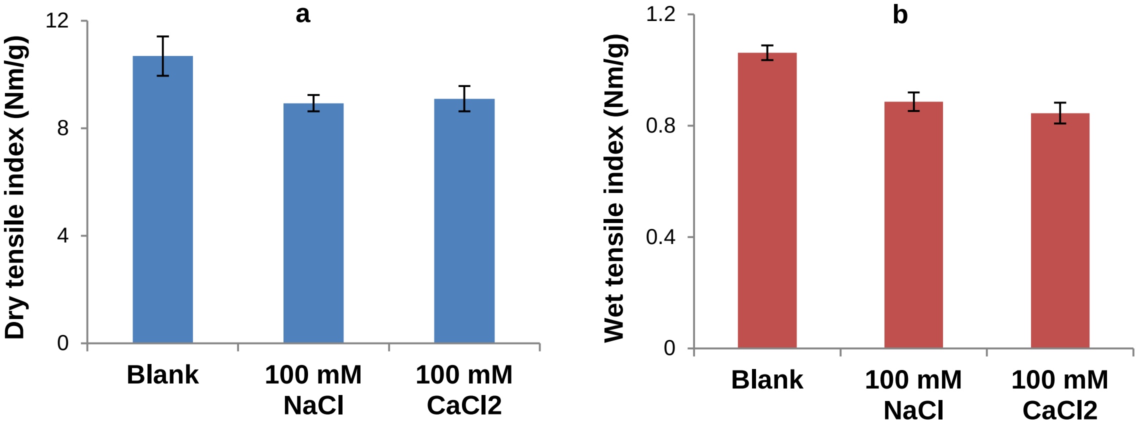

**Figure 6.** Effect of salt concentration in stock on paper strength (without PAE addition). a) Dry strength, b) Wet strength

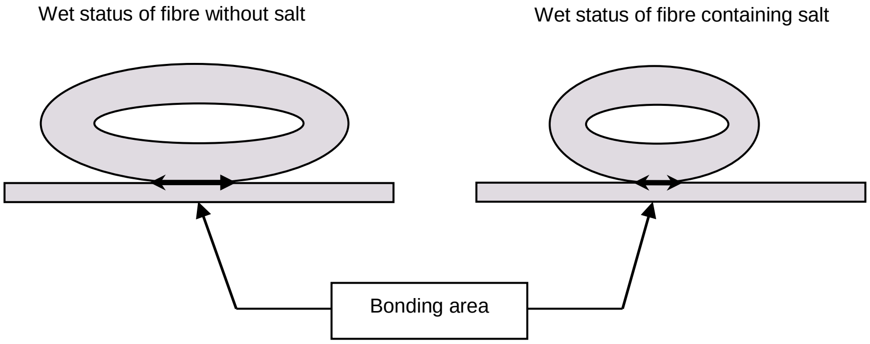

**Figure 7.** Schematic illustration of salt effect on fibres dimension/swelling and bonding area. The geometry is not drawn to scale.

Salt also influences the strength of PAE-strengthened sheets. Figures 8 and 9 show the effect of the NaCl and $CaCl_2$ concentration, respectively, on wet and dry paper strength using a PAE dosage of 10 mg/g. The paper wet strength slightly increased at the low concentration of 10 mM, both for NaCl and $CaCl_2$. Polyelectrolyte adsorption onto surfaces was previously investigated both in model surface and cellulosic fibre (Bates 1969; Enarsson and Wagberg 2008; Solberg and Wagberg 2003), and a maximum in the saturation adsorption of cationic polymer was found at a low NaCl concentration of 10 mM. The increase of strength may be linked to a larger amount of PAE adsorbed on fibres in the presence of salt. A small amount of salt may shield the repulsion between the positively charged groups on the PAE chain and allow the macromolecule to coil up into a tighter, less extended conformation which, in turn, enables the PAE chain attach to the fibres more densely and increase the probability of the azetidinium groups forming covalent bonds with fibres. This mechanism is schematically illustrated in Fig. 10.

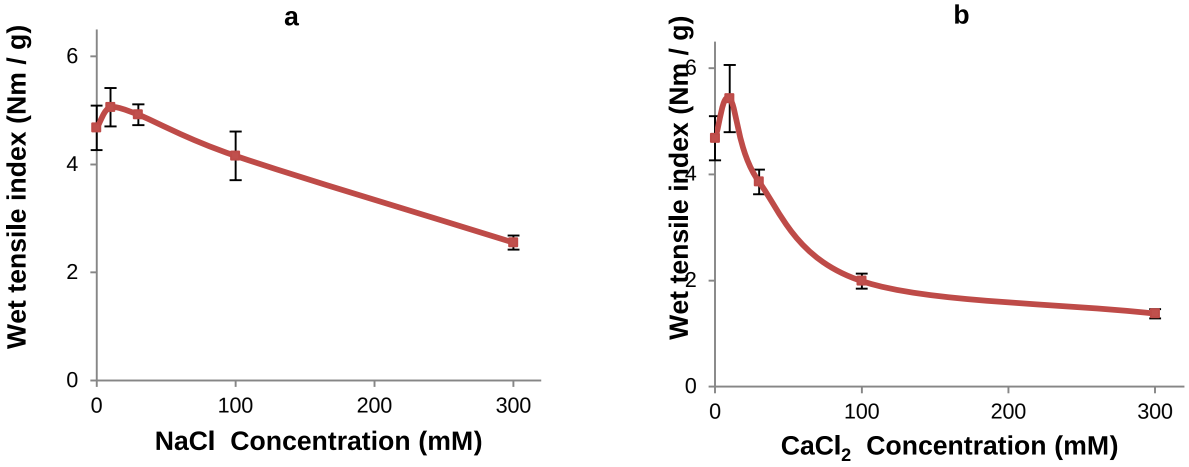

**Figure 8.** Dry tensile index as a function of (a) NaCl and (b) $CaCl_2$ concentration at constant addition level of 10 mg PAE /g dry pulp

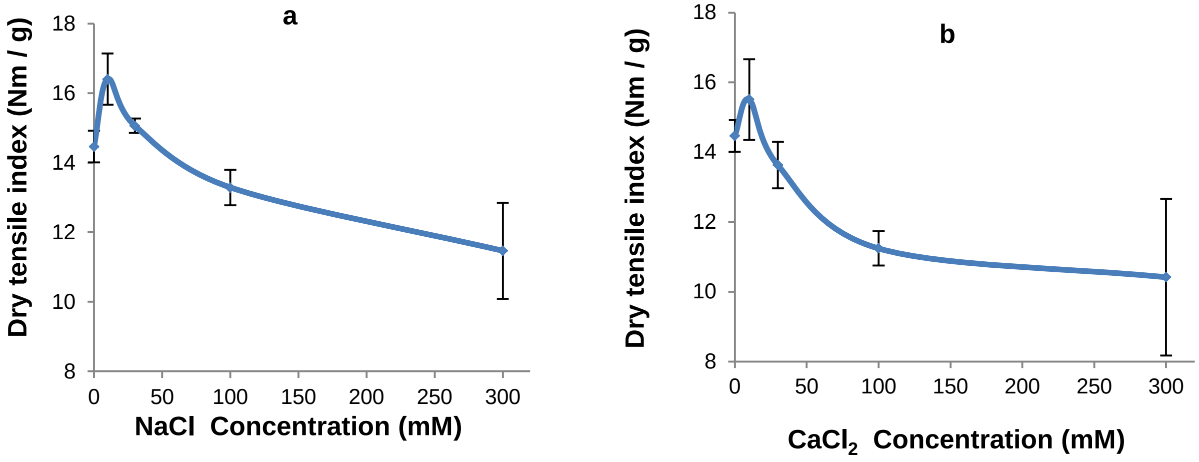

**Figure 9.** Wet tensile index as a function of (a) NaCl and (b) $CaCl_2$ concentration at a constant addition level of 10 mg PAE /g dry pulp

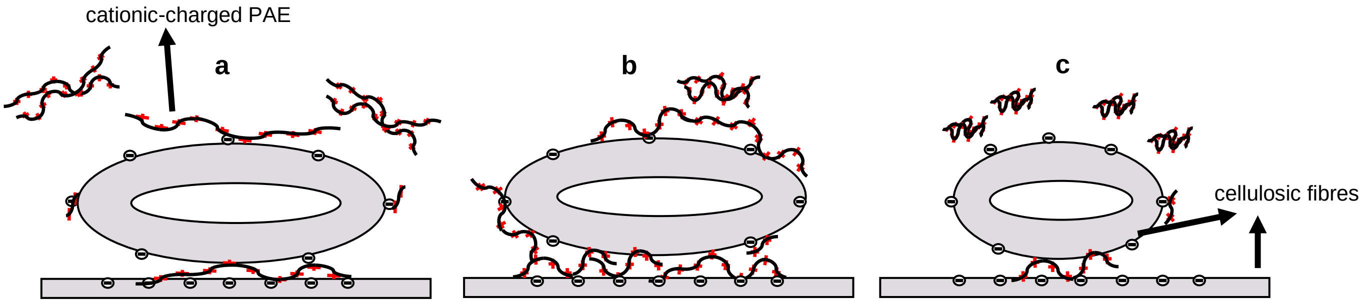

**Figure 10.** Schematic representation of possible mechanism for cationic-charged PAE being adsorbed to cellulosic fibres in different salt concentrations (a) without salt, (b) Low salt concentration, (c) High salt concentration. The figure is not drawn to scale.

Although the paper's tensile index increased at low salt concentration, for concentrations of 30 mM and above, the strength of the paper sheet declined as increasing salt addition screened the electrostatic interaction required for high polymer adsorption (Enarsson and Wagberg 2009). From the perspective of polymer retention, the adsorbed amount of PAE decreases when salts are added (Strazdins 1974). Considering ion exchange between inorganic cations ($Na^+$, $Ca^{2+}$) and polycations from the dissociation of PAE in solution, the high ionic strength significantly affects the PAE adsorption behavior because the increase in the number of small cationic counterions would interfere with the process (Ampulski and Neal 1989). $Ca^{2+}$ ions decreased PAE efficiency more than $Na^+$ did. $Ca^{2+}$ can not only better compete for the fibres carboxyl sites but also decrease the anionicity of fibres, therefore inhibiting PAE retention

## CONCLUSIONS

1. The ability of polyamideamine-epichlorohydrin (PAE) to improve paper tensile strength was investigated by preparing handsheets with bleached eucalyptus kraft pulp. The maximum enhancement of dry and wet strength properties was achieved at different PAE addition levels; the highest wet to dry strength ratio was obtained at 10 mg/g. Above this addition level, the wet strength falls slightly and then remains constant. Fibre flocculation and poor formation of the paper sheets induced by the cationic polymer were observed during the sheet forming process, which explains why higher PAE doses did not improve tensile strength. The repulpability of PAE- strengthened paper revealed a direct link between wet strength and recyclability. The stronger the paper was in a wet state, the harder it became to repulp, being quantified at the same disintegrator energy.

2. The tensile properties of paper formed in various salt-containing environments with and without PAE were examined. In the absence of PAE, both dry and wet paper strength was decreased at high salt concentration. The strength of sheets reinforced by PAE was also affected by the salt concentration in papermaking stock. At PAE dosage of 10 mg/g, low salt (NaCl and $CaCl_2$) concentration at 10

mM enhanced the strength of paper while higher salt addition weakened the paper; this can be explained in terms of ionic strength affecting the polymer's conformation and their adsorption density onto fibres. Ion type and concentration in the papermaking process water influenced the strength development in different manners. Experimental results in this study show the need for new wet strength agents that can be applied in demanding salty conditions while maintaining the product recyclability.

## ACKNOWLEDGMENTS

The financial contribution of Australian Research Council (LP0990526), Visy and Nopco paper technology is acknowledged.

## REFERENCES CITED

Ampulski, R. S., and Neal, C. W. (1989). "The effect of inorganic ions on the adsorption and ion exchange of Kymene 557H by bleached northern softwood kraft pulp," *Nordic Pulp and Paper Research Journal* 04(2), 155-163.

Andreasson, B., Forsstrom, J., and Wagberg, L. (2005). "Determination of fibre pore structure: influence of salt, pH and conventional wet strength resins," *Cellulose*, 12(3), 253-265.

Bates, N. A. (1969). "Polyamide-epichlorohydrin wet-strength resin. 2. A study of mechanism of wet-strength development in paper," *Tappi* 52(6), 1162-1169.

Bates, N. A. (1969). "Polyamide-epichlorohydrin wet-strength resin. I. Retention by pulp," *Tappi* 52(6), 1157-1161.

Bennington, C. P. J., Sui, O. S., and Smith, J. D. (1998). "The effect of mechanical action on waste paper defibering and ink removal in repulping operations," *Journal of Pulp and Paper Science* 24(11), 341-348.

Chan, L. L. (1994). *Wet-strength Resins and their Application*, TAPPI Press, Atlanta, Ga.

Davison, R. W. (1972). "Weak link in paper dry strength," *Tappi* 55(4), 567-573.

Devore, D. I., and Fischer, S. A. (1993). "Wet-strength mechanism of polyaminoamide-epichlorohydrin resins," *Tappi Journal* 76(8), 121-128.

Enarsson, L. E., and Wagberg, L. (2008). "Adsorption kinetics of cationic polyelectrolytes studied with stagnation point adsorption reflectometry and quartz crystal microgravimetry," *Langmuir* 24(14), 7329-7337.

Enarsson, L. E., and Wagberg, L. (2009). "Polyelectrolyte adsorption on thin cellulose films studied with reflectometry and quartz crystal microgravimetry with dissipation," *Biomacromolecules* 10(1), 134-141.

Espy, H. H. (1995). "The mechanism of wet-strength development in paper - A review," *Tappi Journal* 78(4), 90-99.

Espy, H. H., and Geist, G. W. (1993). "Persulfates as repulping reagents for neutral alkaline wet-strength broke," *Tappi Journal* 76(2), 139-142.

Espy, H. H., and Rave, T. W. (1988). "The mechanism of wet-strength development by alkaline-curing amino polymer-epichlorohydrin resins," *Tappi Journal* 71(5), 133-137.
Forsstrom, J., Andreasson, B., and Wagberg, L. (2005). "Influence of pore structure and water retaining ability of fibres on the strength of papers from unbleached kraft fibres," *Nordic Pulp and Paper Research Journal* 20(2), 176-185.
Gardner, D. J., Oporto, G. S., Mills, R., and Samir, M. A. S. A. (2008). "Adhesion and surface issues in cellulose and nanocellulose," *Journal of Adhesion Science and Technology* 22(5-6), 545-567.
Grignon, J., and Scallan, A. M. (1980). "Effect of pH and neutral salts upon the swelling of cellulose gels," *Journal of Applied Polymer Science* 25(12), 2829-2843.
Lindström, T. (1992). "Chemical factors affecting the behaviour of fibres during papermaking," *Nordic Pulp and Paper Research Journal* 7(4), 181-192.
Obokata, T., and Isogai, A. (2007). "The mechanism of wet-strength development of cellulose sheets prepared with polyamideamine-epichlorohydrin (PAE) resin," *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 302(1-3), 525-531.
Obokata, T., Isogai, A., and Onabe, F. (2002). "Studies on the mechanism of wet strength development," *Emerging Technologies of Pulping and Papermaking*, 613-617.
Page, D. H. (1969). "A theory for tensile strength of paper," *Tappi* 52(4), 674-681.
Rowland Stanley, P. (1977). "Cellulose: Pores, internal surfaces, and the water interface," *Textile and Paper Chemistry and Technology*, American Chemical Society, 20-45.
Saito, T., and Isogai, A. (2005). "A novel method to improve wet strength of paper," *Tappi Journal* 4(3), 3-8.
Scallan, A. M., and Grignon, J. (1979). "The effect of cations on pulp and paper properties," *Svensk Paperstidning* 82, 40-47.
Solberg, D., and Wagberg, L. (2003). "Adsorption and flocculation behavior of cationic polyacrylamide and colloidal silica," *Colloids and Surfaces A - Physicochemical and Engineering Aspects* 219(1-3), 161-172.
Strazdins, E. (1974). "Surface chemical aspects of polymer retention," *Tappi* 57(12), 76-80.
Tejado, A., and van de Ven, T. G. M. (2010). "Why does paper get stronger as it dries?" *Materials Today* 13(9), 42-49.
Torgnysdotter, A., and Wagberg, L. (2004). "Influence of electrostatic interactions on fibre/fibre joint and paper strength," *Nordic Pulp and Paper Research Journal* 19(4), 440-447.

Article submitted: October 30, 2011; Peer review completed: December 19, 2011; Revised version received and accepted: January 9, 2011; Published: January 12, 2011.