Understanding Polyamidoamine Epichlorohydrin (PAAE) Retention in Paper

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Polyamidoamine epichlorohydrin (PAAE) is a permanent wet strength resin used in papermaking. When applied to paperboard, some amount of resin is retained in the sheet, and some is lost to the white water. The papermaker usually knows the amount of PAAE charged to the pulp but has no idea how much chemical is retained in the sheet. In addition, the influence of PAAE dosage, freeness, zeta potential, and pulp kappa number variability on PAAE retention is not well understood. Factorial design experiments using unbleached and bleached softwood (loblolly pine) kraft pulps were conducted to understand the factors that affect PAAE retention. The results revealed that PAAE retention, wet tear index, and tensile index not only depended on the PAAE charged of the pulp but also depended significantly on the pulp freeness. In lieu of freeness, zeta potential data can be used to predict PAAE retention. In addition, at similar freeness, bleached pulp has the highest retention of PAAE compared to low and high kappa unbleached kraft pulps. The results also suggest that lignin may have potential as a wet strength agent.

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INTRODUCTION

Wet strength additives are used to improve the resistance of paper to a rupture force in wet environments. These additives change the physical characteristics of paper by providing strength to the sheet when wet. Paper usually retains about 3 to 5% of its dry strength in a wet environment. The use of wet strength chemicals can preserve from 10 to 50% of the sheet's dry strength when wet (Espy 1997; Staib 2005). Common wet strength additives used in the mill are PAAE (polyamidoamine epichlorohydrin) and GPAM (glyoxalated polyacrylamides). PAAE, classified as a permanent wet strength, produces higher wet strength than GPAM, which is classified as a temporary wet strength agent. Studies have shown that with permanent wet strength, as much as 80 to 90% of the wet strength measured after 10 seconds of soaking persists for two hours; however, with temporary wet strength as much as two thirds of the wet strength persists under the same conditions (Avis 1978; Espy 1994; Rita *et al.* 1999; Bajpai 2018; Vähä-Nissi *et al.* 2018; Kumar Jain *et al.* 2022; Francolini *et al.* 2023).

The PAAE chemical structure has amine, azetidinium, and terminal carboxylic acid groups. Although the azetidinium and the amine groups promote the adsorption of PAAE onto the fiber surface, the azetidinium group is the key element in the bonding mechanism between the additive and fiber. During the drying and the heating process, the cationic azetidinium group reacts with the anionic carboxylic group on the fiber to form an ester bond. The resin can also self-crosslink using the azetidinium group, the carboxylic group, and the amino group in its molecules. Both paths, resin-fiber and resin-resin bonding, can impart wet strength to the sheet. Figure 1 shows the covalent bonding formation between the PAAE resin and cellulose (path a) and the self-crosslinking paths (paths b and c) of the resin (Obokata *et al.* 2005; Yoon 2006; Obokata and Isogai 2007). From path a, one can deduct that it will be difficult to wet-strengthen low-yield pulp, due to the low level of carboxylic groups in the pulp (Ntifafa *et al.* 2024)

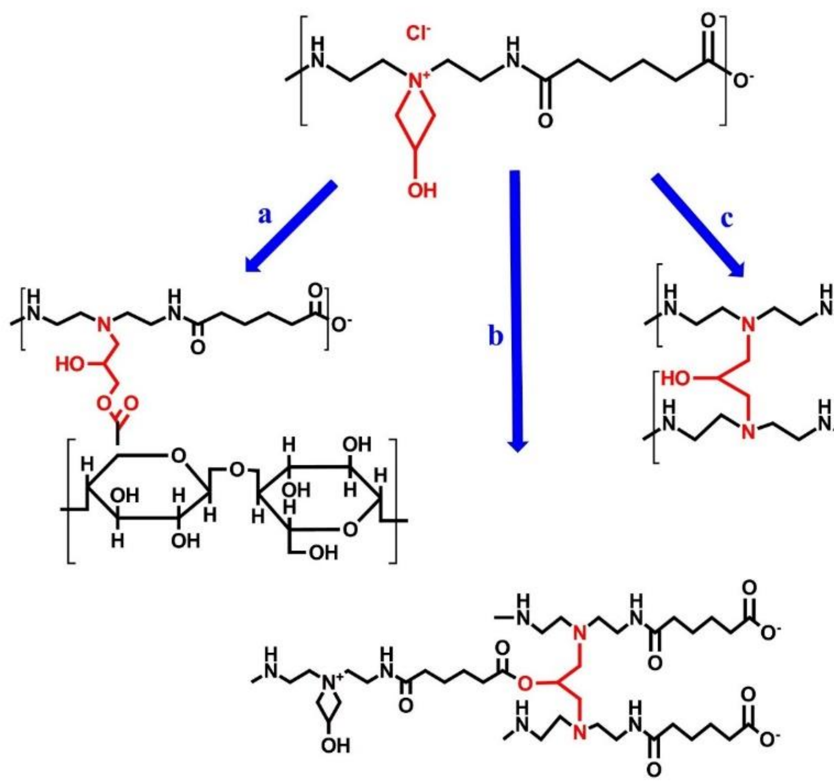


Fig. 1. Structure of PAAE (top), PAAE forming ester bond with cellulose (path a), PAAE main cross linking (path b) and PAAE secondary cross linking (path c)

During the papermaking process, the slurry containing the fibers is dewatered to form a wet fiber network, which is then pressed and dried. Some of the PAAE charged to the pulp is lost during dewatering, and the amount retained in the sheet is not known (Ntifafa *et al.* 2023). In addition, the variables that lead to improved chemical retention are not well known or understood, making it difficult to optimize chemical addition for optimal wet strength performance. Also, PAAE self-reacts (Gao *et al.* 2019; Obokata *et al.* 2005), limiting its retention in multiple passes through the sheet. Thus, white water recirculation has an unknown impact on PAAE retention.

PAAE is known to crosslink fiber with covalent bonds that resist breaking upon wetting. The four main factors that contribute to the development of paper wet-strength when the chemical is added to the pulp are fiber types, concentration of the azetidinium group of the PAAE molecules, adsorption time, and drying conditions (Liu 2004; Obokata *et al.* 2005; Yoon 2006; Obokata and Isogai 2007; Su *et al.* 2012; Onur *et al.* 2019; Weifang Huapu Chemical Co. 2021; Korpela *et al.* 2022). This study examined how the first two factors influence the retention of wet strength agent in the paper. To increase the concentration of the azetidinium group of the PAAE, different PAAE dosages were studied, and to make more carboxylic groups on the fiber surface available, the pulps were refined to different levels of freeness.

The refining process changes the structure of the fiber. During the process, the fiber fibrillates, swells, and the lumen collapses. The resulting pulp from the refining process contains fibers with increased surface area. Fiber modification usually promotes high tensile strength and smoothness of the sheet. In addition, the refiner modifies the freeness of the pulp, generates fines, affects fiber length, and more importantly changes the surface charge of the fibers (Ntifafa 2021; Bhardwaj *et al.* 2007; Banavath *et al.* 2011; Gharehkhani *et al.* 2015; Mandlez *et al.* 2020).

Freeness is one of the most important parameters of the pulp, as it impacts drainage, moisture content leaving the presses (going to the dryer section), and fiber surface zeta potential (SZP). The freeness test is usually performed after the pulp is refined to determine how fast water drains through the pulp. Schopper Riegler (SR) freeness and the Canadian Standard Freeness (CSF) are two main approaches used by papermakers to determine the drainage of the pulp. SR and CSF freenesses are predominantly used in Europe and North America, respectively. A lower number of SR degrees corresponds to faster drainage. On the contrary, a lower number of CSF freeness corresponds to slower drainage. Freeness variations are known to affect the performance especially the speed of paper machine (Hawes and Doshi 1986; Pulp Paper Mill 2014; Bajpai 2018; Ntifafa 2021). In this study, CSF was used after the pulps were refined. Freeness variations along with wet strength dosage variations are studied with different types of pulps.

Factorial design experiments were used to investigate the parameters that influence PAAE retention in paper. PAAE dosage, freeness, zeta potential and kappa are the main factors. The effects of these factors on the tensile index and the wet tear index of the sheets were also investigated. Although wet tensile strength or wet bursting strength were tested, this study also evaluated wet tear strength, as the company's mill operators are specifically interested in this parameter.

EXPERIMENTAL

Reagents

Diethyl adipate 99%, concentrated hydrochloric acid 35 to 38%, absolute ethanol 200 proof, and toluene were supplied by Fischer Scientific (Massachusetts, USA). Concentrated sulfuric acid 95 to 98% was supplied by JT Baker (Pennsylvania, USA). Commercial grade wet strength resin PAAE 20.2% was obtained from a traditional pulp and paper chemical supplier. Loblolly pine pulps were obtained from an operating mill in the Southeast US. The mill used elemental chlorine free (ECF) bleaching sequence D(EP)DD.

Design of Experiment

Minitab 21 (Minitab; State College, PA, USA) software was used to generate mixed- level full factorial design with 2 factors (PAAE charged and freeness) in duplicate;

PAAE retained in the sheet was the response variable. A total of 24 experiments were needed to complete the analysis. The levels are summarized in Table 1:

Table 1. Experimental Design (mixed-level full factorial design)

Factors	Levels			
PAAE Charged (lb/ton) or (ppm)	0	1.5 (750)	3.0 (1500)	6.0 (3000)
Freeness (mL)	300	550	700	-

Papermaking Procedure

Figure 2 illustrates the papermaking and the testing process employed in this work. Unbleached softwood (loblolly pine) kraft pulp obtained from a commercial southeastern US kraft mill was refined, targeting 700, 550, and 300 mL freeness using the Valmet Prolab refiner (Valmet; Espoo, Finland). Each pulp freeness was measured using the Canadian Standard Freeness (CSF) tester according to the TAPPI method T 227 om-21 (2021). The pulp was diluted to 1% consistency, and 500 mL of the resulting pulp was tested on Mütek SZP-10 (Mütek; Herrsching, Germany), to measure the zeta potential of the fiber surfaces. The fiber length and fines percent were determined using TechPap MorFi Neo (TechPap; Grenoble, France).

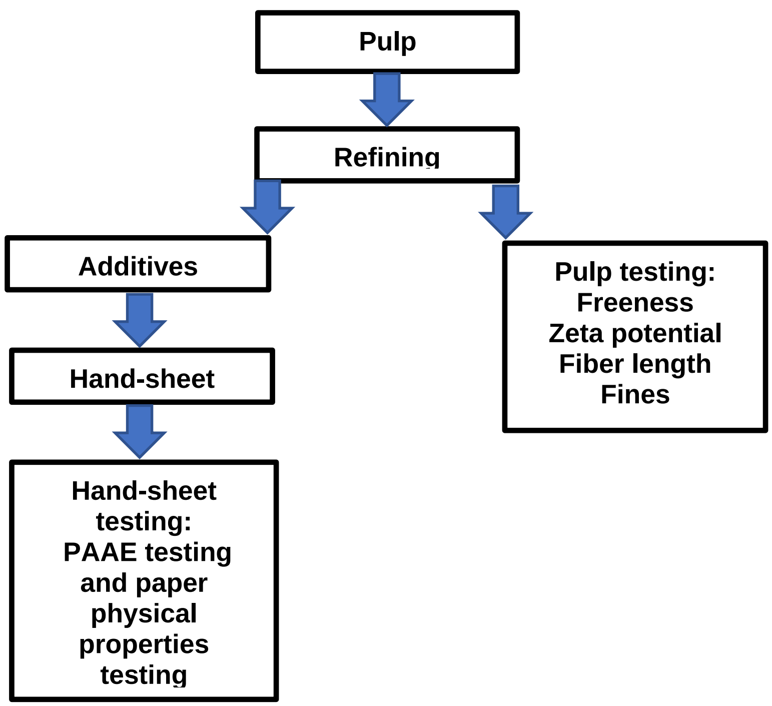


Fig. 2. Flowchart of the testing procedure

PAAE was charged to each type of pulp according to Table 1. Pulp slurry equivalent to 33 g oven dry pulp was added to 2000 mL of water in a Déjà Vu 1387 disintegrator (Déjà Vu Lab and Test Equipment Inc, Mahone Bay, Canada) set at 15000 run cycle; handsheets were made out of the pulps according to the TAPPI method T 205 sp-18 (2018) using AMC hand-sheet molds (Adirondack Machine Corp; Hudson Falls, NY, USA), and pressed twice using a Carver CMG75H-15-PX press (Carver Inc.; Wabash, IN, USA) at 20 tons for 2 minutes. Next, the sheets were transferred to an AMC drum dryer (Adirondack

Machine Corp; Hudson Falls, NY, USA) at 90 °C at 10% speed. The sheets were finally put in the Heratherm OGS400 oven (ThermoFisher Scientific; Waltham, MA, USA) at 105 °C for 5 minutes to cure the wet strength agent.

The tensile index was measured using TAPPI method T 494 om-22 (2022). The wet tear index of the sheets was measured following the TAPPI T 414 om-21 (2021), as modified according to the work by Panek *et al.* (2021). The PAAE retained in the sheet was quantified following the procedure described by Ntifafa *et al.* (2023).

In addition to varying the pulp freeness through refining, the kappa number (lignin content) of the pulp was altered by obtaining a series of pine pulps at different kappa numbers. High kappa, low kappa, and bleached softwood (loblolly pine) kraft pulps were obtained from a commercial southeastern US kraft mill. The TAPPI T 236 om-22 (2022) standard was used to determine the kappa number of the pulps. The pulps kappa numbers were respectively 90.5, 10.7, and 0.1. The pulps were refined, and their freenesses were respectively 535, 545, and 540 mL. Handsheets were made following a factorial design experiment with kappa and PAAE dosage as factors in duplicate (Table 2). Higher dosages of PAAE were not used for this part of the work, because previous work (Ntifafa *et al.* 2023) has shown that at this freeness level, PAAE retention levels off after about 3 lb/ton (1500 ppm) application level.

Table 2. Factors and Ranges

Factors	Levels		
Kappa	0.1	10.7	90.5
PAAE Charged (lb/ton) or (ppm)	1.5 (750)	3.0 (1500)	-

RESULTS AND DISCUSSION

Pulp and sheet test results are summarized in Tables 3 and 4.

Table 3. Freeness, Zeta Potential, Fiber Length, and Fines Percent of Each Pulp before Handsheet Making

Target Freeness (mL)	700	550	300
Measured Freeness (mL)	731	531	280
Zeta Potential (mV)	-28.3	-30.7	-37.3
Fiber Length (mm)	2.2	1.6	1.1
Fines (%)	4.24	5.56	14.95
Conductivity (mS/cm)	1.04	1.17	1.27

Note: the pulp pH is 8.0 with a kappa 9.8

Table 3 shows that the freeness decreased from 731 to 280 mL while the zeta potential increased in absolute value from -28.3 to -37.3 mV. Overall, the negative zeta potential of the fibers increased as the freeness decreased. The opposite trend was found with the fiber length, which decreased from 2.2 to 1.1 mm. The fines increased from 4.24% to 15.0% as the freeness decreased. The refining process is known to generate fines, shorten the average fiber length, and lead to a more negative surface charge (Bhardwaj *et al.* 2007; Banavath *et al.* 2011; Gharehkhani *et al.* 2015; Mandlez *et al.* 2020).

Table 4 shows the response variable values (PAAE retained, tensile index, and wet tear index) that will be the focus of this study. Main effects plots, interaction plots, regression plots, and contour plots were used to understand the significance of the factors (freeness and PAAE dosage), and to determine the best conditions to improve PAAE retention, tensile index, and wet tear index of the resulting paper.

Table 4. PAAE Charged, PAAE Retained, Tensile Index, and Wet Tear Index Results

Freeness (mL)	731	731	731	731	531	531	531	531	280	280	280	280
PAAE Charged (lb/ton) (ppm)	0 0	1.5 750	3 1500	6 3000	0 0	1.5 750	3 1500	6 3000	0 0	1.5 750	3 3000	6 6000
PAAE Retained (lb/ton) (ppm)	0 0	0.91 455	1.62 810	2.14 1070	0 0	1.15 575	2.02 1010	3.33 1665	0 0	1.43 715	2.56 1280	5.35 2675
Basis Weight (g/m^2)	349.3	350.2	348.0	353.2	350.2	349.9	349.4	353.7	351.4	349.0	342.3	343.5
Tensile Index (N.m/g)	35.5	36.3	34.2	36.2	43.4	50.4	49.5	57.5	53.9	51.2	53.4	52.3
Wet Tear Index (mN.m^2/g)	3.7	3.8	4.6	6.6	3.6	4.2	5.6	8.3	4.3	4.7	5.9	7.4

Table 5 shows the p-values for each factor *vs.* responses. The p-values of the interactions between the factors are also shown. All the factors, freeness and PAAE dosage, and their interactions were significant for the responses, as the p-values were less than 0.05. Thus, freeness, PAAE dosage and their interaction were significant for PAAE retained, tensile index, and wet tear index. All data were within 95% confidence intervals.

Table 5. P-values of Freeness and Dosage *vs.* PAAE Retained *vs.* Tensile Index and Wet Tear Index

Responses / Factors	PAAE Retained p-*value*	Tensile Index p-*value*	Wet Tear Index p-*value*
Freeness	< 0.001	< 0.001	< 0.001
PAAE Dosage	< 0.001	< 0.001	< 0.001
Freeness*PAAE Dosage	< 0.001	< 0.001	< 0.001

Effects of Freeness and PAAE Dosage on PAAE Retention

Main effects and interaction plots

The main effect plot of PAAE retained (Fig. 3 a) shows that the PAAE dosage had the most significant effect, followed by freeness. The interaction plot (Fig. 3 b) shows the 6.0 lb/ton (3000 ppm) dosage as the most significant, followed by the 3 lb/ton (1500 ppm) dosage. Both plots show the retention was higher when freeness was lower.

PAAE charged vs. PAAE retained

The slopes in Fig. 4 represent the retention efficiency of the PAAE. The trends of PAAE charge *vs.* PAAE retained show increasing slopes (0.3457< 0.5436 < 0.8842) as the freeness was decreased. The graph shows that the retention of PAAE increased as the freeness decreased.

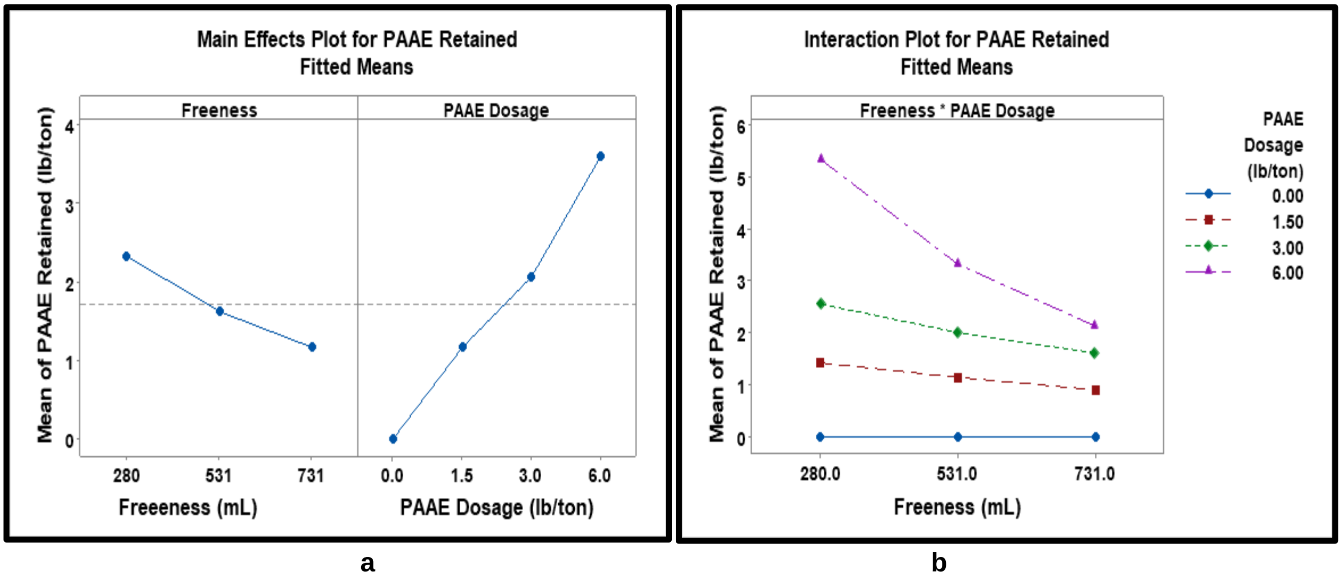


Fig. 3. Main effects of PAAE retained (a) and interaction plots of the PAAE retained (b)

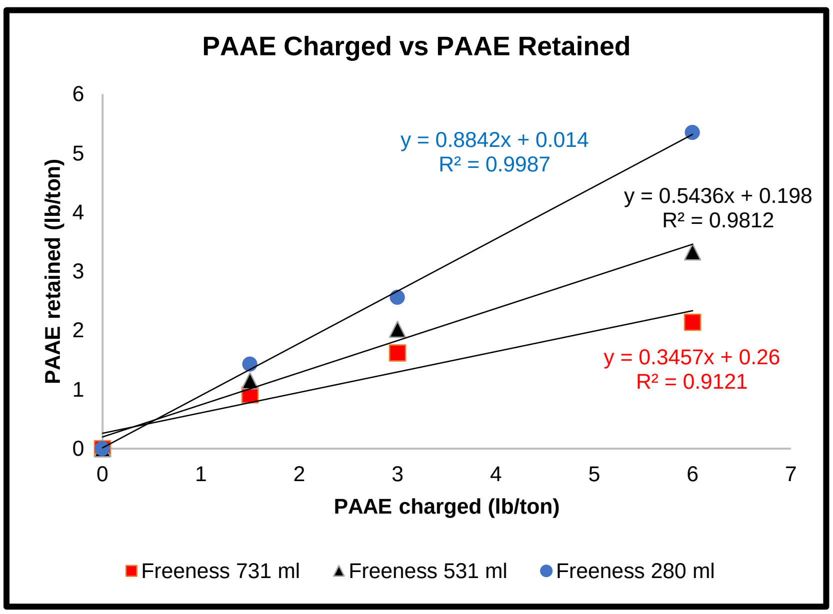


Fig. 4. PAAE charged vs. PAAE retained

Contour plot

The contour plot of PAAE retained (Fig. 5) showed similar trends to the main effects and interaction plots. Overall, the retained amount of PAAE increased when PAAE dosage increased and the freeness decreased. The contour plot also provides more details about the PAAE retained at different target freeness values (300, 550, and 700 mL).

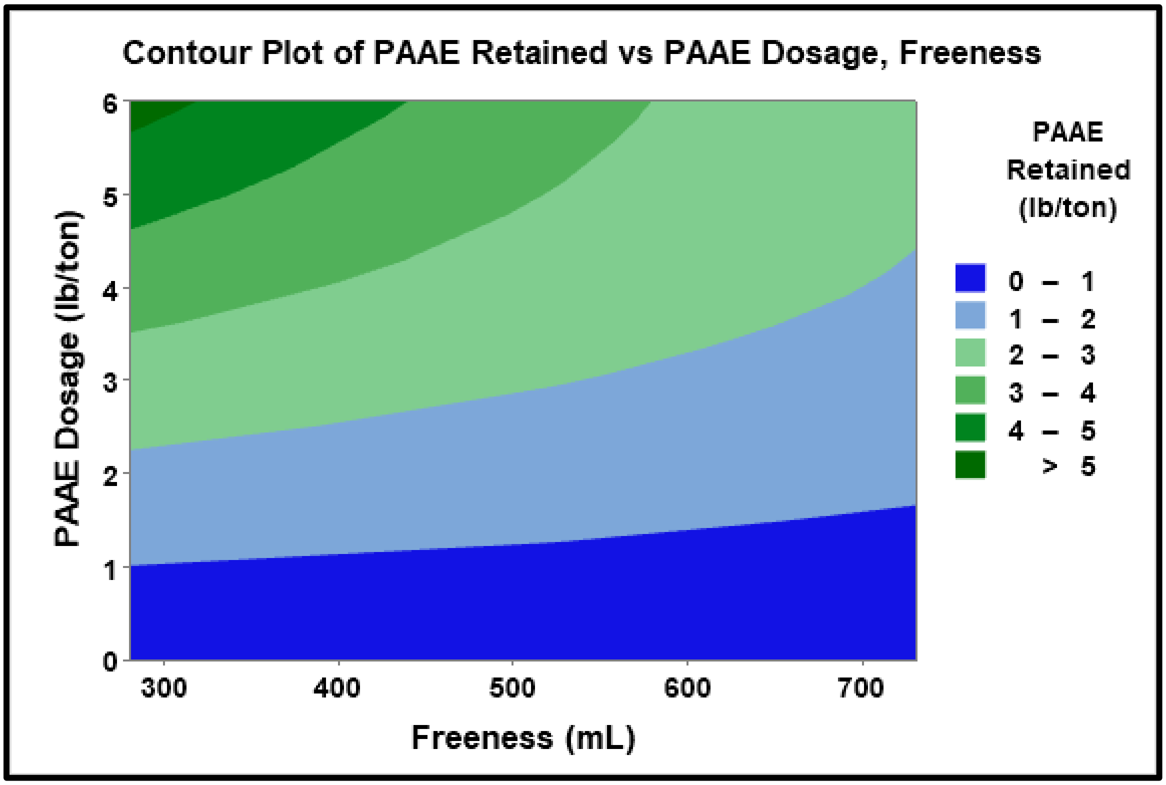


Fig. 5. Contour plot of the PAAE retained as function of freeness and PAAE dosage

The contour plot (Fig. 5) indicates ranges for PAAE retained at various levels of freeness and PAAE dosage. At 300 mL freeness, the highest retained amount of PAAE (>5 lb/ton or >2500 ppm) was achieved with a dosage above 5.8 lb/ton (2900 ppm). The retained amount of PAAE at 550 mL freeness seemed to be moderate, with the retained amount of PAAE interval comprised between 3 to 4 lb/ton (1500 to 2000 ppm) for dosages greater than 5.4 lb/ton (2700 ppm). At 700 mL freeness, the retained amount of PAAE never exceeded 3 lb/ton (1500 ppm) even if the dosage was at 6 lb/ton (3000 ppm); the retention in this case was less than 50%.

The conclusions derived from the PAAE retention (Figs. 2, 3, and 4) are partial, as the information from the effect of freeness and PAAE dosage on the sheet properties is also needed to better understand optimal PAAE application.

Effect of Freeness and PAAE Dosage on Handsheet Physical Properties

Main effects and interaction plots

Referring to the main effect plots of the tensile index (Fig. 6a), freeness had the most significant effect on the tensile index. The interaction plot (Fig. 6b) shows 1.5 lb/ton (750 ppm) dosage as the most significant at 531 mL freeness, followed by the 3lb/ton (1500 ppm) dosage at 280 mL freeness. Both plots show that the tensile index was higher when freeness was lower. Moreover, the main effect plots of the wet tear index (Fig. 6c) show PAAE dosage as the most significant factor, and the interaction plot (Fig. 6d) shows 6 lb/ton (3000 ppm) as the best dosage, followed by 3 lb/ton (1500 ppm).

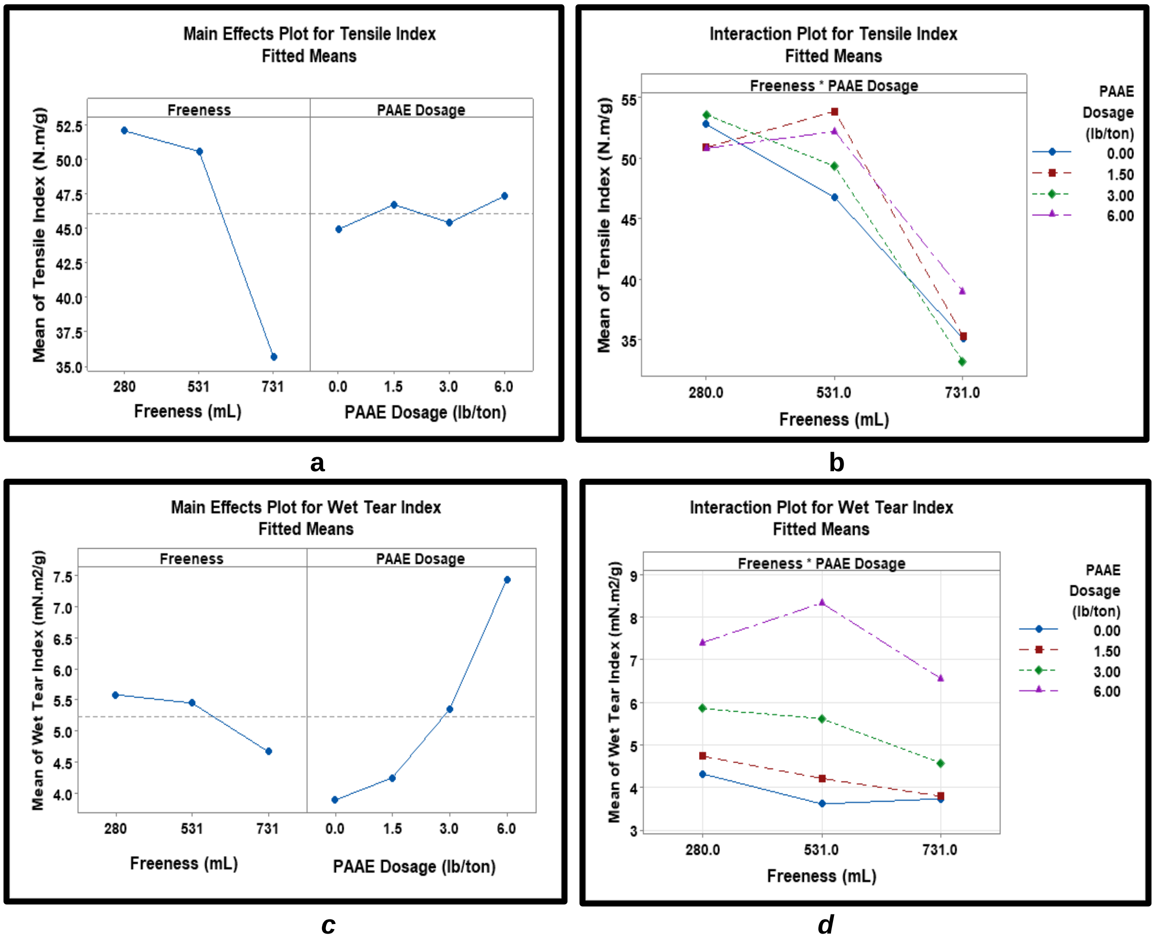


Fig. 6. Main effects and interaction plots of the tensile index (respectively a and b), main effects and interaction plots of the wet tear index (respectively c and d)

PAAE retained vs. tensile index and PAAE retained vs. wet tear index

Figures 7 a and b show PAAE retained *vs.* tensile index and PAAE retained *vs.* wet tear index at different freeness levels. The trends on the tensile index graph were practically flat, while the trends on the wet tear index graph were increasing. Both graphs indicated that more PAAE was retained before 3 lb/ton (1500 ppm), and after 3 lb/ton (1500 ppm) the retained amount of PAAE did not provide a major increase in the response especially for the tensile. Although more data points can be added to determine the level where the amount of PAAE retained plateaus, it was determined that this amount was beyond 6 lb/ton (3000 ppm). At 6 lb/ton (3000 ppm) and 531 mL freeness for example, the amount of retained PAAE was 3.3 lb/ton (1650 ppm). 45% of the chemical was lost. At or above this level of dosage, it can be assumed that PAAE retention is not economically viable.

Figures 7 c and d show PAAE dosage *vs.* tensile index and PAAE dosage *vs.* wet tear index at different freeness levels. The tensile indexes were practically flat, and the wet tear indexes were increasing. The trends are broadly similar to the trends of Figs. 7 a and b as the data points spread from 0 to 6 lb/ton (3000 ppm). Although the PAAE dosage *vs.* tensile and wet tear indexes trends were similar to the PAAE retained *vs.* tensile and wet tear indexes trends, using the PAAE retained data will give better understanding about the percentage of the chemical lost and the actual amount of chemical that is providing wet strength to the sheet. As an example, at a dosage of 6 lb/ton (3000 ppm) at 531 mL freeness

(Fig. 7 c and d), the corresponding retained amount of PAAE was 3.3 lb/ton (1650 ppm) (Fig. 7 a and b). The lost percentage in this case was 45% with only 55% retained PAAE in the sheet.

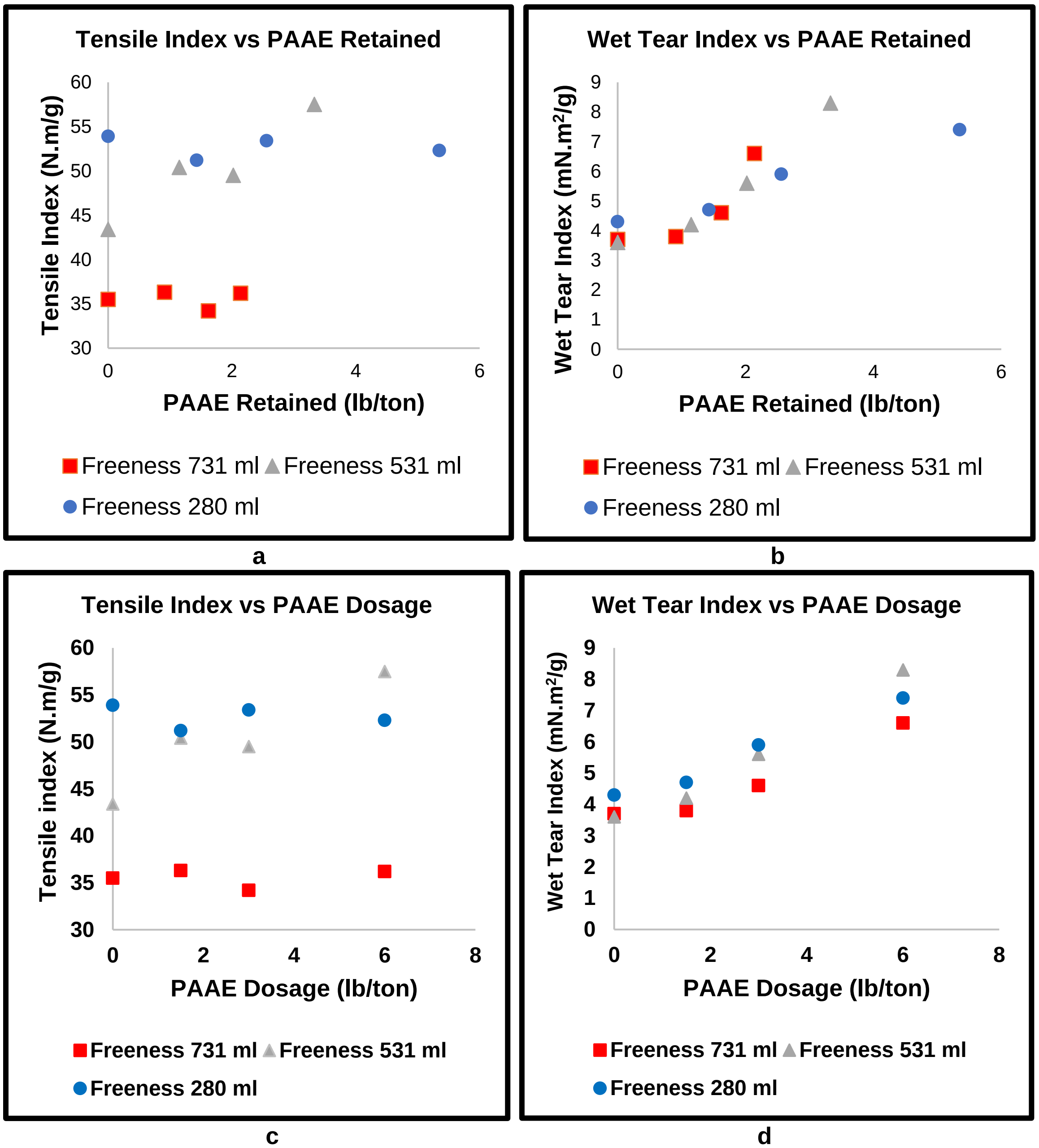
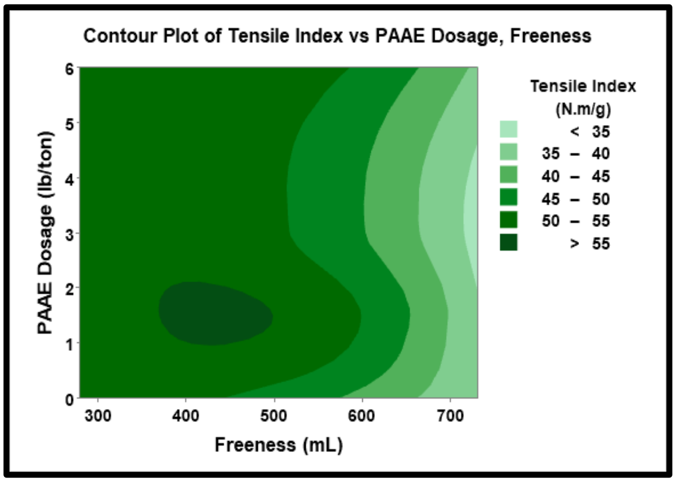


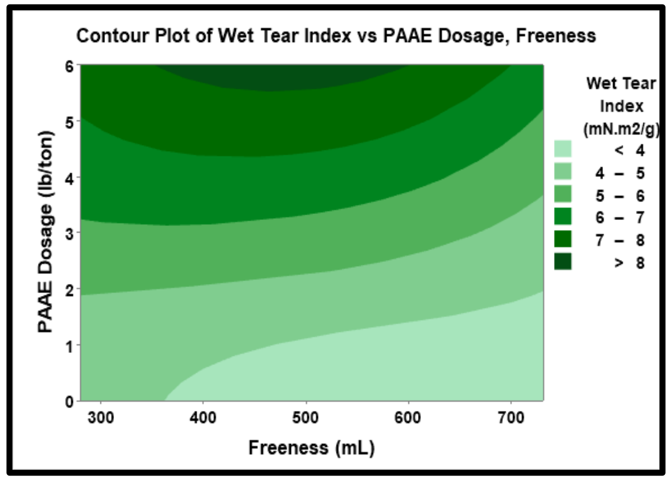
Fig. 7. PAAE retained *vs.* tensile index (a); PAAE retained *vs.* wet tear index (b); PAAE dosage *vs.* tensile index (c); and PAAE dosage *vs.* wet tear index (d)

Contour plots

The contour plots of the tensile and wet tear indexes (Fig. 8) give a broader view of the brackets in which the factors have effect on the responses.



a



b

Fig. 8. Contour plot of the tensile index as function of freeness and PAAE dosage (a), and the contour plot of the wet tear index as function of freeness and PAAE dosage (b)

The tensile index contour plot (Fig. 8, a) overall shows that the tensile increased as the freeness decreased. The highest tensile index (>55 N.m/g) was reached when the freeness was between 370 and 500 mL and the dosage was between 1 and 2.1 lb/ton (500 and 1050 ppm). At 300 mL freeness, the tensile index remained the same, between 50 to 55 N.m/g, even when the PAAE dosage was increased. The data suggest that excessive PAAE usage did not increase the sheet tensile. The tensile index at 550 mL freeness was between 45 and 55 N.m/g for different dosages, while at 700 mL freeness, the tensile index was as high as 45 N.m/g at the highest dosage (6 lb/ton or 3000 ppm).

Compared to the tensile index contour plot, the wet tear index contour plot shows different trends (Fig. 8, b). Overall, the wet tear index increased as the PAAE dosage increased. At 300 and 700 mL freenesses, the wet tear index never exceeded 8 mN.m^2/g. The highest wet tear index (>8 mN.m^2/g) was obtained at 550 mL freeness.

The deductions from Figs. 3, 4 and 5 combined with the conclusions from Figs. 6, 7 and 8 help to understand the performance of PAAE application. Higher freeness (≈700 mL) had the least response results in this study. At higher freeness (≈700 mL), the retained amount of PAAE was less than 3 lb/ton (1500 ppm), the tensile index was less than 45 N.m/g, and the wet tear index was less than 7 mN.m^2/g for the highest dosage of PAAE (6 lb/ton or 3000 ppm). The statistical analysis so far revealed that higher freeness was not the best way to improve the PAAE retention nor the paper properties. The next step is to determine the lowest possible freeness for the best PAAE retention, tensile index, and wet tear index.

The highest retained amount of PAAE (more than 5 lb/ton or 2500 ppm) was observed at lower freeness (≈300 mL) for higher tensile ranged between 50 and 55 N.m/g and for wet tear index close to 8 mN.m^2/g. Although this performance is impressive, the reality is that if the pulp has a very low freeness such as 300 mL, the speed of the paper machine will be considerably reduced for the pulp to have enough time to drain at the forming section. The operation will suffer financial loss due to the speed reduction. The speed reduction is due to low drainage, which in turn is due to the fines generated during the refining process. Fines are fragments of fiber that can pass through a mesh screen of 76 micrometers in diameter (Fischer *et al.* 2017; Winter *et al.* 2021). Excessive fines have a negative impact on the dewatering of the pulp. In the present study, the percent fines increased 169% from the freeness of 531 to 280 mL (Table 3). Some of the impacts of the fines may be mitigated with the addition of drainage aids, but again at a cost.

An additional problem associated with low freeness pulp is that the highly hydrated fiber will result in lower solids webs leaving the press section and entering the dryers. Lower press solids result in increased drying demand, which results in speed reductions for dryer limited machines. Another reason that the papermaker avoids excessive refining is that the process severely shortens, curls, and cracks the fiber (Gharehkhani *et al.* 2015; Mandlez *et al.* 2020). In this study the fiber length was reduced by 31% from 531 to 280 mL freeness (Table 3). Excessive refining makes the fiber less recyclable, thus less sustainable.

Since the statistical results did not recommend higher freeness (≈700 mL), and a sustainable process cannot be achieved with a lower freeness (≈300 mL), an optimized freeness is needed relative to the retained amount of PAAE or the tensile index or the wet tear index based on the need of the papermaker. At a freeness of about 550 mL, the retained amounts of PAAE were around 3lb/ton (1500 ppm) for tensile index ranging between 40 and 55 N.m/g, and the highest wet tear index was obtained (more than 8 mN.m^2/g). However, the decision to use different freeness or dosage depends on the paper grade or desired types of properties improvement (tensile, wet tear) that the papermaker is targeting. As an example, the dosage of 1.5 lb/ton (750 ppm) PAAE corresponds to the highest tensile increase, but no significant gain was obtained when the dosage is increased to 3 or 6 lb/ton (1500 or 3000 ppm) (Fig. 6, a). On the contrary, the dosage 6lb/ton (3000 ppm) led to the highest wet tear index (Fig. 6, c). Depending on the paper grade, 3lb/ton (1500 ppm) can be used to increase the tensile strength without wasting a large amount of the chemical and at the same time increase the wet tear. Lastly, the PAAE charged *vs.* tensile index and PAAE charged *vs.* wet tear index graphs (Fig. 7) revealed that more PAAE was retained before 3 lb/ton (1500 ppm).

Alternative to Freeness Test to Predict PAAE Retention

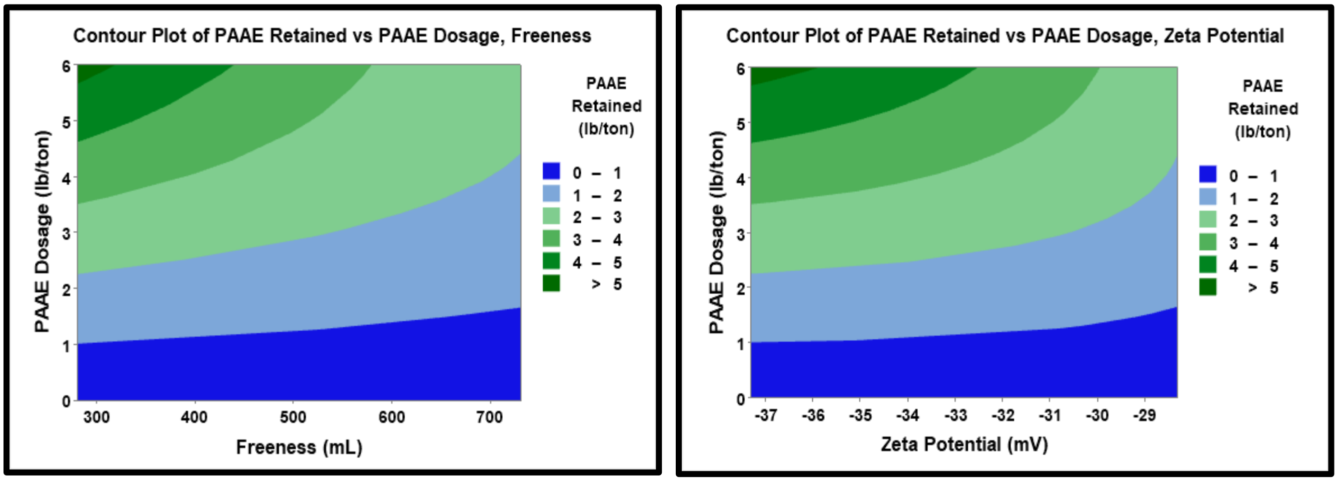
Freeness and PAAE dosage have been shown to be significant with respect to PAAE retention. The freeness test can be tedious, time consuming, or unavailable. To investigate whether factors other than freeness can be used to predict the PAAE retention, the above data analysis was redone using the corresponding zeta potentials in place of the freeness (Table 3).

The p-values (Table 6) when using zeta potential as factor are all less than 0.001, which was similar to those with freeness as factor.

Table 6. P-values of PAAE Retained Using Freeness and PAAE Dosage vs P-Values of PAAE Retained Using Zeta Potential and PAAE Dosage

	PAAE Retained
Factors	*p-values*
Freeness	< 0.001
PAAE Dosage	< 0.001
Freeness * PAAE Dosage	< 0.001
Zeta Potential	< 0.001
PAAE Dosage	< 0.001
Zeta potential * PAAE Dosage	< 0.001

The contour plot trends were also similar (Fig. 9), which suggested that instead of the freeness test, the zeta potential measurement can be used to predict PAAE retention. As the freeness decreases, the fiber is more open and fibrillated leading to higher surface charge (Bhardwaj *et al.* 2007; Banavath *et al.* 2011; Gharehkhani *et al.* 2015).



a b

Fig. 9. Contour plot of the PAAE retained as function of freeness and PAAE dosage (a), and contour plot of the PAAE retained as function of zeta potential and PAAE dosage (b)

The contour plots suggest that there was a strong correlation between the freeness and zeta potential. The evidence is also in line with published finding about the effects of refining on pulp surface charges (Banavath *et al.* 2011; Bhardwaj *et al*. 2007; Xu *et al.* 2017). Overall, as the retained amount of PAAE increases, freeness decreases. This relationship can be explained by the structural change of the fiber after the refining process. The obtained highly fibrillated fiber retains more water resulting to freeness reduction. Moreover, the fiber charge increases after the refining process (Table 3) and favors the attraction and retention of PAAE.

INFLUENCE OF KAPPA ON PAAE RETENTION, TENSILE INDEX, AND WET TEAR INDEX

Kappa number or kappa basically measures the remaining lignin content in the pulp after wood chips digestion. Higher kappa number translates to higher lignin content (Chai *et al.* 2000; Małachowska *et al.* 2020).

Table 7. PAAE Charged, PAAE Retained, Tensile Index, and Wet Tear Index Results

Kappa	90.5	90.5	10.7	10.7	0.1	0.1
PAAE Charged (lb/ton) **(ppm)**	1.5 750	3 1500	1.5 750	3 1500	1.5 750	3 1500
PAAE Retained (lb/ton) **(ppm)**	0.54 270	0.83 415	1.09 545	2.32 1160	1.22 610	2.61 1305
Basis Weight (g/m^2)	350.8	354.7	352.1	353.2	352.9	355.3
Tensile Index (N.m/g)	54.0	65.5	43.0	50.6	59.7	64.7
Wet tear Index (mN.m2/g)	8.9	11.0	2.2	4.1	16.6	18.4

A new set of experiments was conducted to understand how PAAE retention is affected by high kappa, low kappa, and bleached (no kappa) pulps. The pulp kappa numbers were respectively 90.5, 10.7 and 0.1. The zeta potential values were respectively -34, -46 and -51 with pH 8.5, 8.2 and 7.3. Table 7 summarizes PAAE dosages and sheet properties data.

The responses in this section of the study were PAAE retained, tensile index, and wet tear index (Table 7). The following p-values tables, Pareto charts, and contour plots give clarity on the significance of the effects of kappa on PAAE retention, tensile index, and wet tear index.

Effects of PAAE and Lignin on PAAE Retention

P-values and Pareto chart

Table 8 shows the p-values for each factor and their interaction.

Table 8. P-values of Kappa and Dosage vs PAAE Retained and Percent PAAE Retained

	PAAE Retained
Factors	p-values
Kappa	< 0.001
PAAE Dosage	< 0.001
Kappa*PAAE Dosage	<0.001

All the factors, kappa and PAAE dosage, and their interactions were significant for the PAAE retained, as the p-values were less than 0.05. The Pareto chart (Fig. 10) indicated that dosage had the most significant effect, followed by kappa.

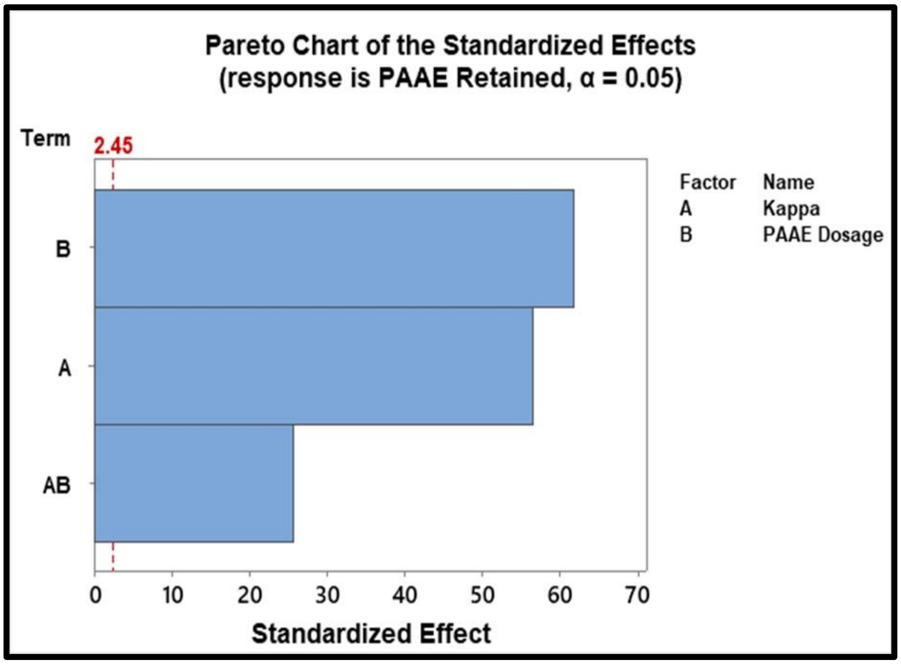


Fig. 10. Pareto chart of PAAE retained using kappa and dosage as factors

Contour Plots

Analysis of the contour plot (Fig. 11) shows how retained amount of PAAE changed as the kappa and the dosage changed. The trends in the contour plot show that more PAAE was retained as the dosage increased and the kappa decreased.

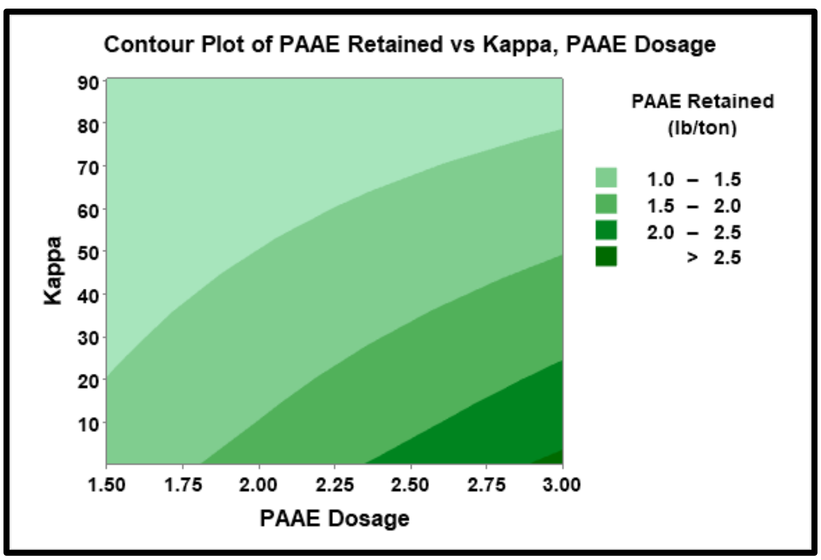


Fig. 11. Contour Plot of PAAE retained as function of PAAE dosage and kappa

At the highest kappa (90) and highest dosage (3 lb/ton or 1500 ppm), less than 1.0 lb/ton (500 ppm) of the additive was retained. This observation simply means that more than 65% of the chemical was lost at high kappa and high dosage. As mentioned earlier, four main factors contribute to the development of sheet wet strength when PAAE is added to the pulp (fiber types, concentration of the azetidinium group, adsorption time, and drying conditions) (Liu 2004; Obokata *et al.* 2005; Yoon 2006; Obokata and Isogai 2007; Su *et al.* 2012; Onur *et al.* 2019; Weifang Huapu Chemical Co. 2021; Korpela *et al.* 2022). In this study, the pulps (fiber types) were treated in similar conditions; however, the results were not the same. The results suggest that at high kappa, the amount of lignin is high in the sheet and the availability of the carboxylic groups on the fiber (hemicellulose, cellulose) is low or hindered.

The low availability of carboxylic groups in high kappa pulp to react with PAAE can be explained by the presence of lignin-carbohydrate complexes (LCC). Eight different types of LCC bonds are known: benzyl ether, benzyl ester, glycosidic, phenyl glycosidic, hemiacetal linkage, acetal linkage, ferulate ester, and diferulate ester. The hydrolysis of these bonds, especially ester-based bonds, during the kraft pulping process or during the bleaching process will make available carboxylic groups on hemicellulose and cellulose on lower kappa and bleached pulps. In such cases, the electrostatic attraction between the anionic carboxylated group of the fiber and the cationic azetidinium group of PAAE would be favored (Chen 2014; Nishimura *et al.* 2018; Tarasov *et al.* 2018; Terrett and Dupree 2019; Cui *et al.* 2022; Susi *et al.* 2023).

Effects of PAAE and Lignin on Tensile Index and Wet Tear Index

PAAE application is known to increase sheet tensile and wet strength. Lignin can provide wet strength to the sheet, and in some cases, it can reduce its tensile strength (Zhang *et al.* 2013; Joelsson *et al.* 2020; Mattsson *et al.* 2021; Huang *et al.* 2023; Francolini *et al.* 2023). In this part of the experiment, the focus is on knowing individual or combined effects of PAAE and lignin on both tensile index and wet tear index.

The p-values in Table 9 show that kappa and PAAE dosage were both significant for the tensile index and the wet tear index (p-values < 0.05); however, their interactions were not significant (p-values > 0.05).

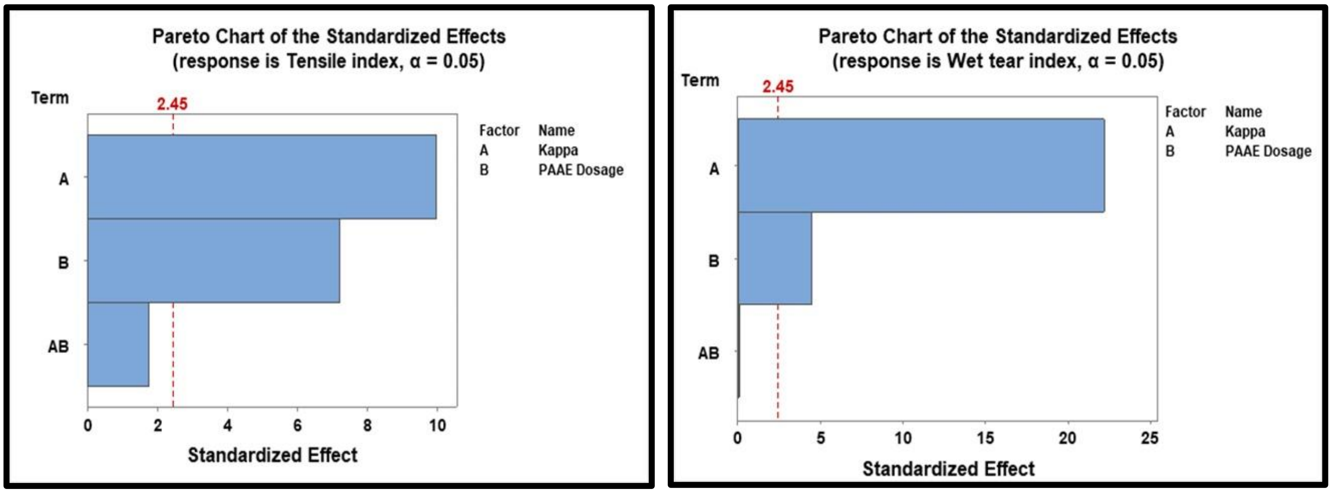
Table 9. P-values of Kappa and Dosage *vs.* Tensile Index and Percent Wet Tear Index

	Tensile Index	**Wet Tear Index**
Factors	*p-value*	*p-value*
Kappa	< 0.001	< 0.001
PAAE Dosage	< 0.001	0.004
Kappa*PAAE Dosage	0.129	0.945

The tensile index and wet tear index Pareto charts in Fig. 12 provide more details on the effects of the factors.

Pareto charts

The Pareto chart of the tensile index (Fig. 12, a) indicated that kappa was the most significant factor with respect to the tensile strength, followed by dosage. Similar to the tensile index Pareto chart, wet tear index Pareto chart (Fig. 12, b) indicated that kappa was the most significant factor followed by dosage.

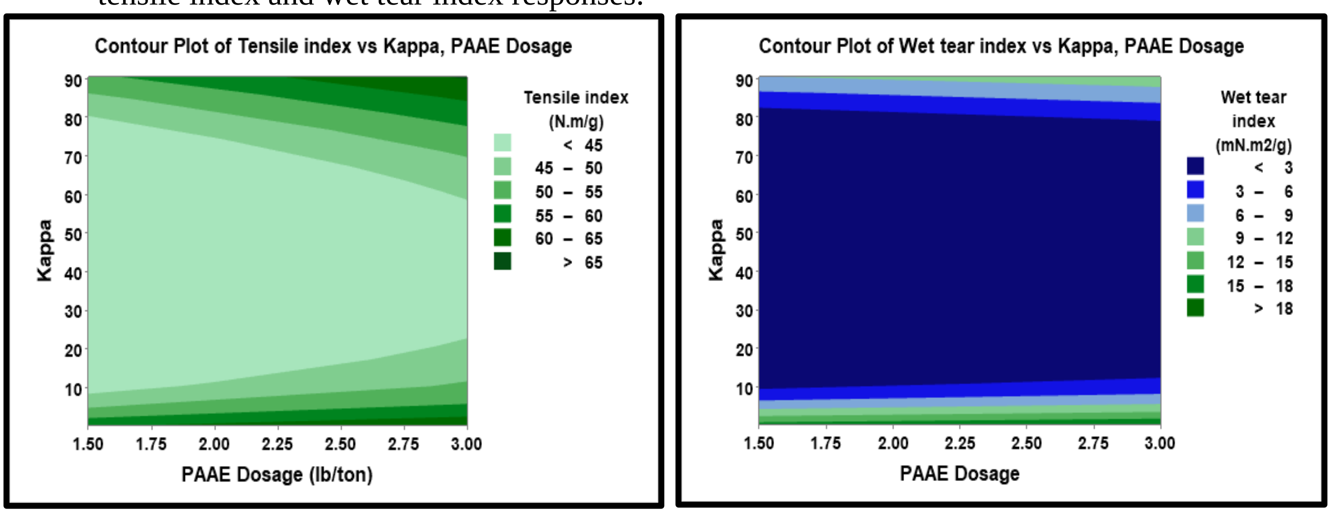


a b

Fig. 12. Pareto charts of tensile index (a) and wet tear index (b) using kappa and dosage as factors

Contour plots

The contour plots in Fig. 13 indicate how kappa and PAAE dosage affected the tensile index and wet tear index responses.



a b

Fig. 13. Contour plots of tensile index (a) and wet tear index (b) as function of PAAE dosage and kappa

At a glance, the contour plots of the tensile index and the wet tear index exhibited their highest values at both extremes of kappa, whether the PAAE dosages were increased or not. At lower kappa, the tensile index and the wet tear index increased when the dosage increased. The trends suggest that the wet strength agent not only improves the wet strength of the sheet but also the tensile strength (dry).

At higher kappa, the tensile index and the wet tear index increased. It was previously shown from Fig. 11 that at higher kappa more than 65% of the additive was lost and the interaction between the dosage and kappa was not significant (Table 8). In deduction, lignin, which is dominant at high kappa, mainly provided high wet tear and tensile strength for the sheet (Joelsson *et al.* 2020; Huang *et al.* 2023). On the contrary, when the lignin is removed, the retained amount of PAAE increases due to the availability of carboxylic groups on hemicellulose and cellulose, resulting in high wet tear of the sheet (Ntifafa *et al.* 2024).

The results suggest that to provide wet strength to the sheets, PAAE is needed in the absence of lignin or lignin is needed in the absence of PAAE. The effect of these two individual factors was more significant than their interaction or combination (Table 8). In addition, Table 7 shows that the sheets with 10.7 kappa number retained more PAAE compared to those with 90.5 kappa, but their wet tear indexes were lower. Comparing only the amount of PAAE retained in the sheets could be misleading, as one type of samples had more lignin than other. One can deduct that the combination of lignin and small amount of PAAE in the sheet with kappa number 90.5 provided more wet strength.

The results indicated that lignin could provide significant wet strength to paper. The application of natural or modified lignin as wet strength agent needs to be investigated. Biomaterial based wet strength agent made from lignin would be more sustainable and suitable for recyclable or repulpable paper products. Concerning the interaction of lignin and PAAE, which is ineffective or not significant in this study, interaction p-values > 0.05 (Table 8), a possible retention agent may be used to increase the amount of the PAAE retained in the sheet at higher kappa. The physical properties of the resulting paper should be investigated.

The limitations of other researchers in the use of lignin as a wet strength agent are not fully known. More investigations are needed to uncover these limitations; however, the use of lignin as wet strength may affect the brightness of the paper as lignin tends to be brown. Economic viability is also needed to understand if lignin is a better choice over PAAE. The stabilities of the sheets' wet strength over a certain period also need to be compared between lignin based wet strength and PAAE based wet strength. Overall, in this study, it was found that high presence of lignin will occupy cellulose fiber functional groups, and the PAAE retention will not be enhanced.

This study did not investigate the mechanism by which lignin increases wet tear strength; however, according to Mattsson *et al.* (2021), the wet strength development can be explained by the stronger bonding between the fiber due to the interdiffusion of lignin macromolecules.

In this study, handsheets were mainly used to understand the retention of PAAE. The white water was not reused to retain the PAAE that drained through the wire. Often in an industrial application, white water recirculates, allowing the chemical multiple times to be retained in the sheets. Unfortunately, PAAE self-reacts, resulting in the deactivation of the chemical (Gao *et al.* 2019; Obokata *et al.* 2005; Ntifafa *et al.* 2024). Therefore, PAAE does not have as many opportunities to be retained in the sheet as compared to other wet end chemicals during recirculation.

CONCLUSIONS

1. Polyamindoamine-epichlorohydrin (PAAE) is an effective wet strength resin. In this study, statistical approaches were used to understand how retained amount of PAAE is affected when the pulp freeness, zeta potential, kappa number, and the PAAE dosage vary. The results indicated that additive retention increases as the freeness decreases.

2. PAAE retention was found to improve wet tear index and moderately improve tensile index.
3. The study showed that refining to low freeness led to highly negative zeta potential, which can be used instead of freeness to control retained amount of PAAE.
4. At high kappa, retained amount of PAAE in the sheet decreases. Interaction between the additive and fiber is limited due to the presence of lignin, leading to low retention.
5. Sheets' wet strength targets can be achieved by high lignin content at low PAAE dosage, or high PAAE content at low kappa.
6. Lignin is a potential wet strength agent; however, its application needs to be further investigated for the development of a biobased wet strength agent.
7. If possible, a retention aid to retain PAAE at high kappa may be used, and the resulting effects on the physical properties of the paper (wet strength and tensile) should be studied. In addition, PAAE retention using diverse types of recycled pulps needs to be investigated.
8. In this study, only softwood (SW) pulp was used. More study needs to be done to understand how 100% hardwood (HW) or blended SW/HW will affect PAE retention and sheet properties.

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