Wet-strength mechanism of polyaminoamide-epichlorohydrin resins

David I. Devore and Stephen A. Fischer

ABSTRACT: The NMR spectra of polyaminoamide-epichlorohydrin (PAE) solutions and the mechanical tensile properties of paper handsheets made with PAE resins are consistent with a wet-strength mechanism based on a homo-crosslinked resin bound only by electrostatic and hydrogen bond forces to the paper fibers. From ^{1}H and ^{13}C NMR spectra collected during the thermosetting of PAE resin, no evidence can be found for covalent bonding between the PAE resin and model compounds having the same cellulosic functional groups found in paper. The thermosetting reaction rate is dependent upon the temperature, pH, and carboxylate anion present in solution. The tensile strengths of paper handsheets made with PAE resins obey an additivity rule consistent with the behavior of independent networks of resin and paper fibers. This additivity rule does not apply to wet strength agents known to covalently bond to paper fibers, but it does apply to PAE in the presence of carboxymethylcellulose.

KEYWORDS: Additives, bibliographies, epichlorohydrin, nuclear magnetic resonance, polyamines, wet strength.

The chemical mechanism by which polyaminoamide-epichlorohydrin (PAE) resin produces wet strength has not been resolved despite a number of investigations going back almost to the introduction of these products over 30 years ago *(1)*. The PAE resins have become the most commercially important thermosetting products for the production of wet-strengthened paper in neutral-to-alkaline pH paper furnishes.

Two distinct mechanisms by which PAE resins may impart wet strength to paper have been proposed *(2, 3)*: (a) formation of an independent resin–resin "homo-crosslinked" network (resin–resin covalent bonding) or (b) formation of a resin–cellulose "co-crosslinked" network (resin–cellulose covalent bonding). The evidence supporting the first mechanism, resin–resin covalent linkages only, is that PAE resins readily thermoset to form coherent elastic films *(4)*. Also, adsorption of the cationic PAE by various pulps is governed by electrostatic forces, as demonstrated by the effects of added salts and free (anionic) carboxyl group concentrations on the pulp fibers *(5)*, and by the direct relationship between the PAE resin's performance and the zeta potential *(6)*. PAE resin does not bind radioactively labeled glucoside, a monomeric model for cellulosic hydroxyl groups, which is indicative of the absence of covalent ether linkages between PAE and the cellulosic fibers *(4)*.

In support of the second, "co-crosslinking" mechanism, the formation of covalent ester linkages between PAE resin and cellulosic carboxyl groups can be inferred from the analysis of handsheet data and solubility data *(7)*, and from single fiber–fiber bond strengths *(8)* for PAE in the presence of carboxymethylcellulose. Pyrolysis gas chromatographic data may also be indicative of ester bond formation between the resin and carboxylic groups in PAE-treated paper *(9)*. The two mechanisms are not mutually exclusive, however, and other handsheet data have been interpreted as supporting a combination of the two processes *(10)*.

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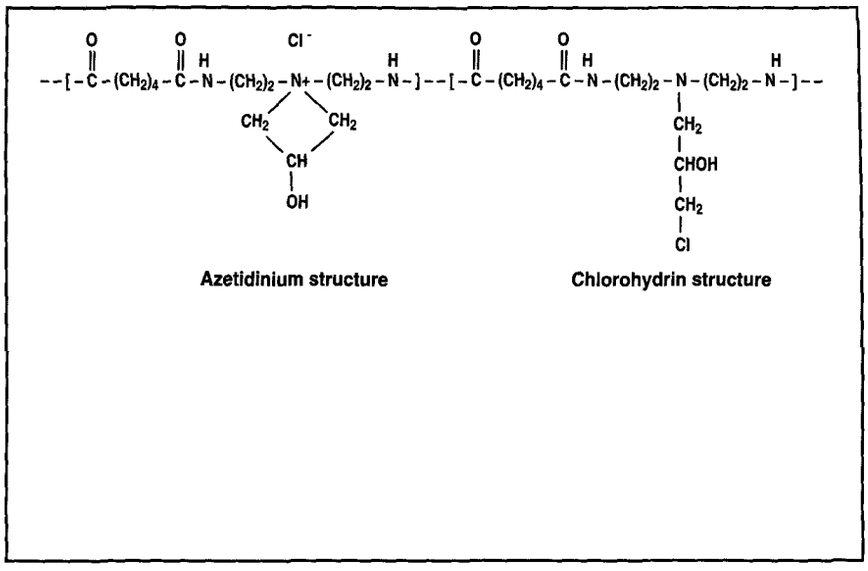
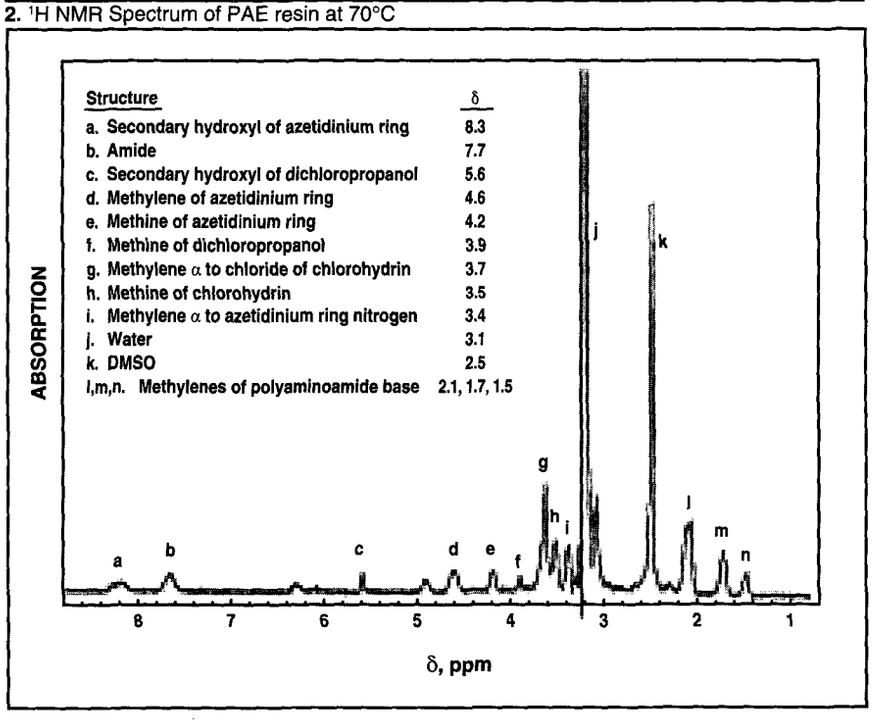
In this paper, we report direct spectroscopic evidence of the chemical processes which do and do not occur during the PAE thermosetting reaction, and we relate this to new observations on the mechanical properties of PAE-treated paper handsheets. The functional groups in the PAE resin are identified and quantified by ^{1}H and ^{13}C NMR and by wet analytical methods. The kinetics of the thermosetting reaction are followed by ^{1}H NMR in the presence of model cellulosic and resin functional groups so that the preferred kinetic pathways can be distinguished. Wet and dry tensile strength data from cured handsheets made in this laboratory or reported in the literature are then analyzed in terms of a physical network model to account for the chemical and mechanical properties imparted by PAE and other wet-strength resins.

1. Molecular composition of PAE resin



2. ^{1}H NMR Spectrum of PAE resin at 70°C



Experimental

Polyaminoamide-epichlorohydrin resin preparation

The preparation of the PAE resin followed standard methods *(11, 12)*. The resin was prepared by first synthesizing an aqueous polyaminoamide by a condensation reaction of dibasic ester and diethylene triamine, and then reacting this linear polymer with epichlorohydrin. The epichlorohydrin reaction was allowed to proceed until a viscosity corresponding to a molecular weight of about 10^4 Daltons was reached, after which the reaction was stopped by acidifying the aqueous resin solution.

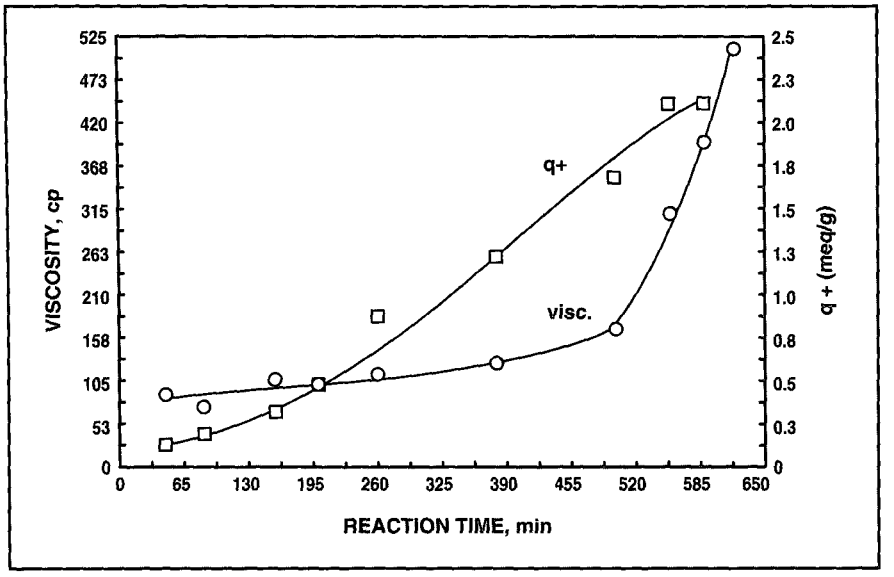
NMR experiments

A Varian 4VXR-400S NMR spectrometer equipped with a Sun 4/110 computer was used to generate the ^{1}H and ^{13}C spectra. Data reported represent an average of three experiments repeated under identical conditions.

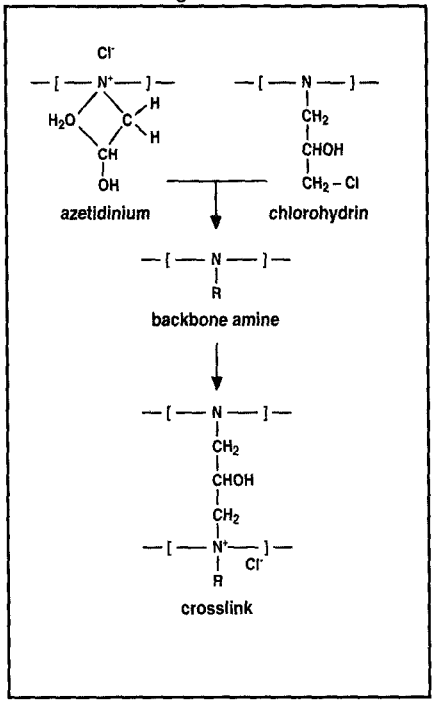
To follow thermosetting kinetics, the PAE resin was adjusted to pH 7.95 with aqueous sodium hydroxide and added to deuterated dimethyl sulfoxide (DMSO) to produce a final resin solution concentration of 0.40% by weight. This solution was placed in an NMR tube, heated to 70°C within 2 min, and proton spectra were obtained at approximately 10-min intervals at a constant 70°C.

To determine the reactivity of PAE with model cellulosic and resin functional groups, the compounds acetic acid, ethanol, and dibutyl amine were each diluted in deuterated DMSO to 0.6% by weight. Aliquots of 0.02 g of each solution were added to 3.32 g of the 0.40% PAE resin solution, such that the final concentration of the model compounds was approximately 0.004%. These solutions were placed in NMR tubes and spectra were obtained at 25°C for proton identification. The samples were then heated to 70°C and proton spectra were obtained over time at this temperature.

3. Development of cationic charge and viscosity during PAE synthesis



4. PAE crosslinking reaction scheme



To determine the presence of any ester formation between PAE and carboxylates, acetic acid was added to the PAE resin solution, the pH was raised to 8.0 with aqueous sodium hydroxide to form sodium acetate, and the solution was diluted with DMSO to a final concentration of 0.4% PAE resin and 0.08% sodium acetate. The ^{1}H and ^{13}C NMR spectra were then obtained at 25°C and at 70°C.

Handsheet preparation

All paper handsheets were made using an 8 in. Mark IV dynamic handsheet mold *(13)*. The handsheets were dried at 105°C for 10 min and cured at various temperatures for periods specified in the data tables. Strips of 2.54 cm x 20 cm were cut from the cured sheets and soaked in deionized water for 1 h before determining their wet tensile strengths on an Instron tester. Dry tensile strengths for the sheets were also determined. Multiple handsheets were made under identical conditions in order to obtain statistically reliable tensile strengths (standard deviations were less than 10% of the average tensile strengths for a given handsheet treatment).

Results and discussion

Structure of PAE resin

The molecular composition of PAE illustrated in **Fig. 1** was based on the ^{1}H NMR spectra of the PAE resin shown in **Fig. 2**, along with titration data to be discussed below. The functional groups present were identified by peak assignments based on literature references *(14, 15)* and ^{1}H NMR spectra of the raw materials used to make the resin. These peak assignments are summarized in Fig. 2.

Carr *et al. (14)* reported an epoxide structure on the backbone of the PAE resin (complex multiplets between 3.2 and 2.5∂); however, methylene epoxide protons were not observed in our ^{1}H NMR spectra. The absence of epoxide groups in the PAE resin was confirmed by titration with perchloric acid *(16)*. The absorptions at 5.6∂ and 3.9∂ were from the secondary hydroxyl proton and methine in dichloropropanol, a reaction by-product of epichlorohydrin commonly found in PAE resins *(17)*.

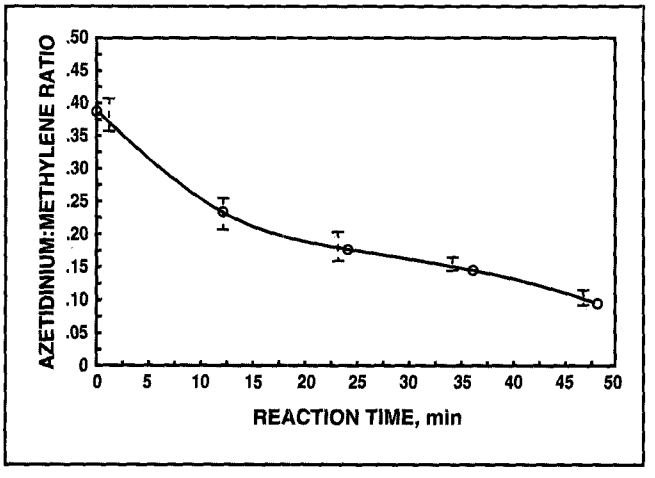
The cyclic azetidinium content in the PAE resin was 16.0% (wt:wt). This was calculated by taking the ratio of the integrated peak areas of the secondary hydroxyl proton of the azetidinium ring to the secondary hydroxyl proton of the dichloropropanol, and multiplying by the concentration of dichloropropanol; the dichloropropanol concentration was separately determined to be 10.15% (wt:wt) by gas chromatography *(18)*. The azetidinium salts were formed by the cyclization of the chlorohydrin groups during the synthesis reaction *(19, 20)*.

Titration of PAE resin with the potassium salt of polyvinylsulfate (PVSK) *(21)* was indicative of a distribution of 46% quaternary and 54% tertiary amines. This was calculated from the ratio of cationic charge at pH 10.0 to that at pH 3.0 *(17)*. Titration for amines *(22)* confirmed that the resin did not contain primary and secondary amines. The tertiary amines were therefore mono-chlorohydrins, while the non-azetidinium quaternary amines were di-chlorohydrins or their crosslinked residues.

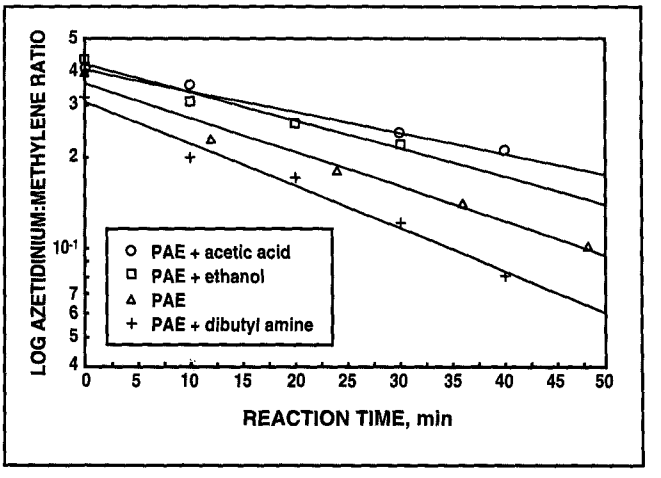
From the PVSK titrations, amine titrations, and ^{1}H NMR spectra, a 3.4:1 mole ratio of tertiary amines to azetidinium in the PAE resin was calculated. This was based on a repeat unit molecular weight of 305.5 for the chlorohydrin and azetidinium structures shown in Fig. 1.

During the course of the PAE synthesis reaction, the quaternary charge (q+) density of the resin increased continuously, as determined by PVSK titration (**Fig. 3**). Crosslinking, as

5. Reaction of azetidinium in PAE resin at 70°C



6. First order plot



indicated by the rise in viscosity with synthesis reaction time (Fig. 3), occurred when the azetidinium ring or the chlorohydrin groups reacted with the tertiary amines on the polyaminoamide backbone, as illustrated in **Fig. 4**. The incorporation of epichlorohydrin in the resin was sufficient, based on initial reactant concentrations, to assure that each secondary nitrogen in the polyaminoamide backbone had reacted with at least one epichlorohydrin molecule.

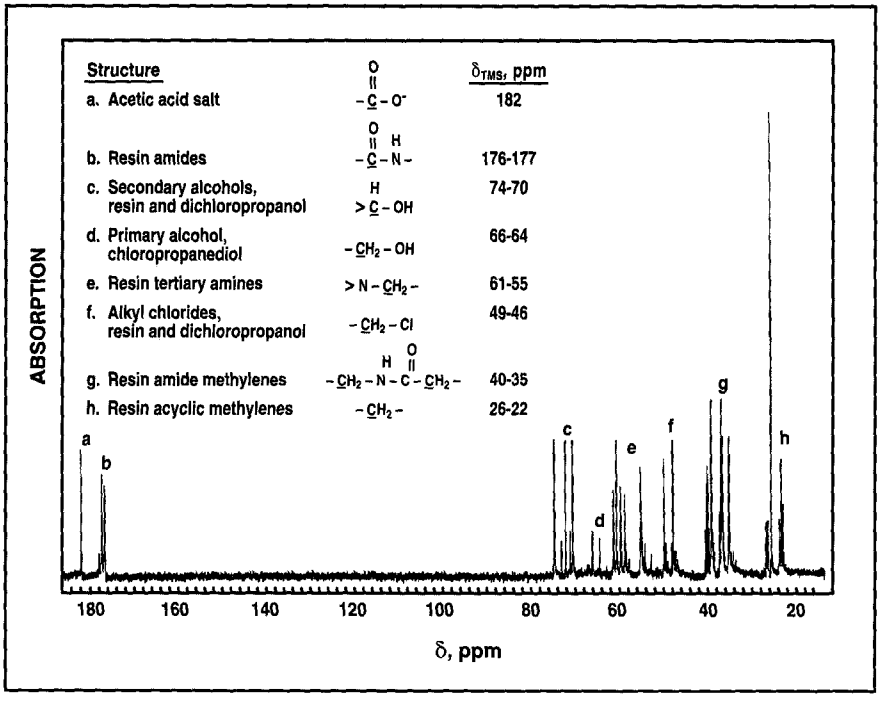
Kinetics of PAE thermosetting reactions

From the change in azetidinium concentration observed by ^{1}H NMR as a function of reaction time (**Fig. 5**), the thermosetting reaction of PAE resin was found to follow pseudo first order kinetics. In Fig. 5, the integrated area of the azetidinium secondary hydroxyl proton (8.3∂) in the PAE resin was compared to the integrated area of the backbone polyaminoamide methylene proton (1.7∂) which remained constant during the course of the experiments. To determine the order of reaction and the observed rate constants, k_{obs} the data in Fig. 5 were replotted using the integrated rate Eq. 1 and 2 for first order and second order reactions *(23)*, respectively:

$$A = A_0 \exp(-kt) \quad (1)$$

$$1/A = 1/A_0 + kt \quad (2)$$

7. ^{13}C NMR Spectrum of PAE resin



where

A = azetidinium-to-methylene ratio

k = rate constant

t = time

The first order plot (**Fig. 6**) was linear (correlation coefficient = 0.90) with a slope corresponding to an observed rate constant, k_{obs}, of 4.58×10^{-4} s^{-1}; the second order plot was nonlinear. The reaction was taken to approximately 75% completion, as calculated from the difference between the starting and final azetidinium-to-methylene ratios.

To account for the observed pseudo first order behavior, the thermosetting of the PAE resin was ascribed to the opening of the azetidinium group such that a tertiary amine group was left in its place and a new di-chlorohydrin quaternary group was formed with a formerly tertiary amine group to create a crosslink (Fig. 4). This process resulted in the disappearance of azetidinium groups while a steady-state tertiary amine concentration was

maintained, in accord with pseudo first order kinetic behavior. A more detailed analysis of the kinetics is given in the Appendix.

Functional group effects on PAE thermosetting

^{1}H NMR and reflectance FT-IR spectra were run on mixtures of PAE resin and cellulose, hydroxyethyl cellulose, and carboxymethyl cellulose in an effort to obtain direct evidence of covalent bonding. However, poor resolution of the ^{1}H NMR spectra made proton absorptions difficult to interpret, and the reflectance FT-IR experiments lacked sufficient sensitivity to detect changes in PAE spectra due to paper interfacial interactions.

Therefore, ^{1}H NMR experiments were conducted with PAE resin mixed with either acetic acid, sodium acetate, or ethanol in order to determine the reactivity of the azetidinium ring with compounds which modeled the carboxyl and hydroxyl functionalities found in paper. Also, the reactivity of the PAE resin mixed with dibutyl amine was studied to determine the effect of an alternative amine source on the azetidinium ring opening. In these experiments, the proton absorption of the secondary hydroxyl on the azetidinium ring was again followed as a function of reaction time at 70°C.

The azetidinium ring-opening kinetics in the presence of the model compounds were again pseudo first order, as shown in Fig. 6, with linear correlation coefficients between 0.93 and 0.94. The observed pseudo first order reaction rate constants for the azetidinium reaction in the presence of the acetic acid, ethanol and diethanol amine, obtained from the slopes of the lines, were 2.82, 3.66, and 5.66 x$10^{-4}s^{-1}$, respectively.

From the observed rate constants, it was clear that the thermosetting reaction was retarded by acetic acid and ethanol while dibutyl amine increased the reaction rate. Acetic acid protonated the resin backbone tertiary amines, which in effect reduced their nucleophilicity and inhibited their reactivity with the azetidinium rings. The effect of ethanol was similarly ascribed to the inhibitory formation of hydrogen bonds with the backbone tertiary amines.

Since a small amount of dibutyl amine was added to the PAE resin and, as a result, the overall amine-to-azetidinium molar ratio was not significantly changed (3.4:1 to 3.5:1), the reaction rate was expected to be close to k_{obs}, for the PAE reaction alone. The much faster rate observed resulted primarily from the effect of the increased basicity on de-protonation of the backbone amines.

In the ^{1}H NMR experiments, no changes were observed in the proton absorptions of the RCOO*H* proton (12.0∂) or the RO*H* proton (4.2∂), and therefore it was concluded that no covalent bonding reactions took place between the azetidinium ring and acetic acid or ethanol. The reactivity of the RO*H* proton was determined by subtracting the area contributed by the methine proton, determined in prior experiments, from the total area at 4.2∂, since the hydroxyl proton in ethanol and the methine proton in azetidinium overlapped in the ^{1}H NMR spectra. The proton absorption for dibutyl amine (R_2N*H* at 2.5∂) could not be followed because of interference from the DMSO signal. The reactivity of the azetidinium ring in the presence of sodium acetate at pH 8.0 was too rapid to permit sufficient ^{1}H NMR data to be collected for determination of the rate constant. This was a surprising result, given the acetic acid result above, and initially suggested that covalent ester bonds could be forming. To determine the nature of this effect, ^{13}C NMR were run on the PAE-sodium acetate solution.

In the ^{13}C NMR spectra, shown in **Fig. 7**, no evidence of ester groups was found. The peak assignments are summarized in Fig. 7. The functional groups were identified by ^{13}C NMR spectra of the raw materials used to make the resin. This confirmed that no covalent bonds formed between azetidinium and carboxylate groups under thermosetting conditions. The increased azetidinium reactivity observed in the ^{1}H NMR experiment was ascribed to a salt effect *(24)*, where an increase in ionic strength of the solution caused an increase in the reaction with backbone tertiary amines. Such a salt effect could account for the enhanced performance of PAE resins by carboxymethylcellulose in paper handsheets *(7)*.

Handsheet tensile properties

In addition to the direct spectroscopic evidence above, analysis of the data from handsheets made in this laboratory **(Table I)** and reported in other studies *(10, 25)* **(Table II)** provided support for a strictly physical, noncovalent interaction between PAE resins and paper. The tensile strengths for handsheets made with PAE resins and polyethylenimine (PEI) were observed to follow a simple additivity rule for mixtures, often observed in polymer blends *(26)*, which took the form:

$$DT_r = (WT_r - WT_b) + DT_b \qquad (3)$$

where

WT = wet tensile

DT = dry tensile

r = resin-treated handsheet

b = blank (untreated) handsheet.

The term $WT_r - WT_b$ represented the tensile strength of the resin network in the absence of the paper fibers.

This additivity rule held for PAE and PEI regardless of the curing times and temperatures or the resin dosages. All of the data for PAE resins and PEI were plotted in **Fig. 8** as DT_r (additivity rule) versus DT_r (experimental), and the correlation coefficient was 0.993. PEI was studied because under standard handsheet making conditions its structure limited it to noncovalent hydrogen bonding and electrostatic bonding to paper *(3, 27)*.

In contrast to PAE and PEI, large deviations from the additivity rule were found for handsheets made with melamine-formaldehyde *(10)*, polyacrylic acid covalently bonded via

ester linkages with cellulose *(25)*, PEI covalently bonded via imine linkages to oxidized cellulose *(25)*, or monomeric thiol-carboxylic acid fiber crosslinking agents *(25)* (Table II). Thus, resins which developed wet strength by resin-cellulose covalent bonding did not follow the additivity rule. Previous studies of the wet-strength mechanism for melamine-formaldehyde resins were inconclusive *(28, 29)*, but the deviations from the additivity rule suggested that covalent bonding was a significant factor.

The additivity rule for tensile strengths was also found to hold for handsheets made with PAE and carboxymethylcellulose (**Table III**) *(30)*. This was taken as evidence of strictly electrostatic interactions between the PAE and the carboxymethylcellulose which would enhance resin adsorption *(31, 32)* and hence the relative effectiveness of a given resin dosage *(5)*. The carboxymethylcellulose may also enhance the wet strength via a catalytic salt effect on the curing of the PAE, in accord with the above NMR observations.

Conclusions

Quaternary salt and chlorohydrin structures were identified by ^{1}H NMR as the reactive functional groups in the PAE resin. It was determined from ^{1}H NMR spectra that 16% of the quaternary salt groups were azetidinium. Also, the azetidinium-to-backbone amine crosslinking reaction was pseudo first order with respect to azetidinium concentration. The azetidinium reaction rate was increased by the addition of a nucleophile (dibutyl amine) and was greatly increased by a salt effect with sodium acetate, but was retarded by proton-donating acetic acid and ethanol.

The ^{1}H NMR and ^{13}C NMR spectra excluded covalent bonding between the PAE resin and sodium acetate, acetic acid, or ethanol. The cellulosic carboxyl and hydroxyl groups in paper were expected to be equally nonreactive with PAE resin.

I. Handsheet tensile strengths for PAE and PEI resins

Resin	Dosage, % on fiber	Cure time, min	Wet tensile, kPa	Dry tensile, kPa	Additivity dry tensile[a], kPa
Blank[b]	-	2 wks	0.76	75.4	-
PAE[b]	0.4	2 wks	12.90	84.8	87.6
Blank[c]	-	4 wks	1.45	71.4	-
PAE[c]	0.4	4 wks	12.50	79.2	82.5
Blank[d]	-	30	1.45	70.8	-
PAE[d]	0.2	30	11.90	79.1	81.2
PAE[d]	0.4	30	13.60	79.2	82.9
PAE[d]	0.6	30	17.70	81.6	87.0
PAE[d]	0.8	30	22.40	91.4	91.7
Blank[e]	-	40	0.48	53.9	-
PAE[e]	0.5	40	8.83	57.2	62.2
PEI[e]	0.5	40	8.79	67.3	62.2

[a] Calculated dry tensile from the additivity rule, Eq. 3.
[b] Bleached kraft furnish, cured @ 25°C and 50% RH.
[c] Bleached kraft furnish, cured @ 25°C and 50% RH.
[d] Bleached kraft furnish, cured @ 105°C.
[e] 100% secondary fiber furnish, cured @ 70°C and 50% RH.

II. Literature data for handsheet tensile strengths

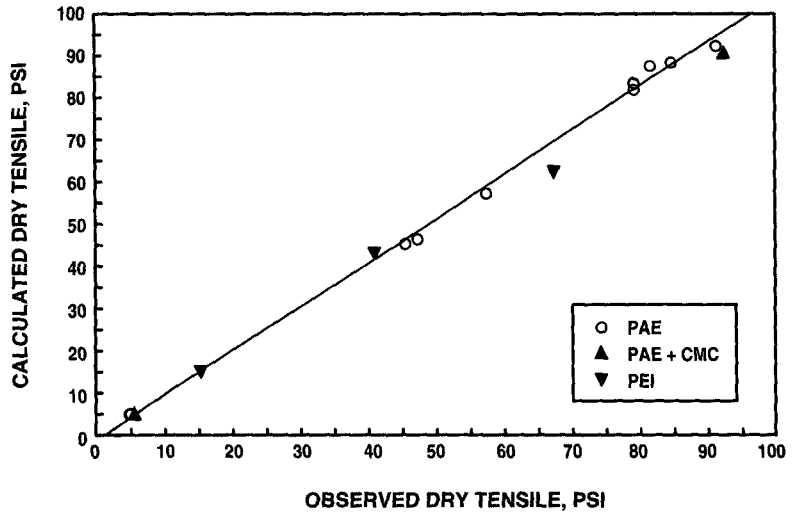
Resin	Dosage, % on fiber	Wet tensile, N·m/g	Dry tensile, N·m/g	Additivity dry tensile[a], N·m/g
Blank[b]	-	1.3	36.6	-
PAE[b]	0.5%	10.1	45.4	45.4
PAE[b]	1.0%	11.2	47.2	46.5
PEI[b]	1.0%	7.9	40.6	43.2
MF[b,c]	2.0%	14.4	55.8	46.4
MF[b,d]	2.0%	18.2	70.2	63.2
MF[b,e]	2.0%	18.9	72.4	67.4
MF[b,f]	2.0%	20.4	76.8	72.5

Resin	Wet tensile, kN/m	Dry tensile, kN/m	Canculated dry tensile[a] kN/m
Blank[g,h]	0.42	14.70	
PEI[g,h]	1.27	15.10	15.6
PEI[g,i]	6.00	11.40	20.3
Blank[g,j]	1.40	6.50	
poly(acrylic acid)[g,j]	3.30	7.40	8.4
Dithioglycolic acid[g,j]	2.30	4.80	7.4
Dithiobutyric acid[g,j]	2.34	5.00	7.4

[a] Calculated dry tensile from the additivity rule, Eq. 3
[b] Reference *(10)*; [c] 650 mL CSF; [d] 500 mL CSF; [e] 350 mL CSF; [f] 200 mL CSF;
[g] Reference *(25)*; [h] unbleached kraft; [i] oxidized unbleached kraft; [j] unbleached kraft cured at 170°C.

The tensile strengths of PAE treated handsheets followed a simple additivity rule in accord with a strictly physical network interaction of cured resin and cured paper fibers. Similarly, tensile data from handsheets treated with PEI, a polymer which could not form covalent bonds to the paper under the experimental conditions tested, was also found to follow

8. Calculated dry tensile vs. observed dry tensile from Tables I,II, and III



III. Effect of carboxymethylcellulose (CMC) on PAE handsheets

Resin	Wet tensile, km[a]	Dry tensile, km[a]	Calculated dry tensile[b], km[a]
Blank[c] (avg.)	0.15	4.23	-
0.45% PAE[c]	0.94	4.74	5.02
0.45% PAE + 0.3% CMC[c]	1.10	5.30	5.18
0.75% PAE[c]	1.12	4.98	5.20
0.75% PAE + 0.3% CMC[c]	1.10	5.40	5.18
	Wet tensile, kPa	Dry tensile, kPa	Additivity dry tensile[b], kPa
Blank[d]	1.45	70.8	-
0.2% PAE[d]	11.90	79.1	81.2
0.2% CMC[d]	1.54	71.7	-
0.2% PAE + 0.2% CMC[d]	19.80	92.5	89.9

[a] Breaking length
[b] Calculated dry tensile from the additivity rule, Eq. 3
[c] Reference *(30)*
[d] This paper, 30 min cure at 105°C

the additivity rule, while resins which were known to form covalent bonds to paper fibers did not follow the additivity rule. This was taken as confirmation that PAE did not form covalent bonds with paper cellulosic functional groups.

Thus, the mechanism by which PAE resin produced wet strength was essentially one of resin homo-crosslinking, with electrostatic interactions between the PAE and paper governing the resin's absorption and hence the dose-response behavior. ■

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Appendix

The rate of the thermosetting reaction for PAE resin is given by the number of crosslinks [*XL*] formed per unit time:

$$d[XL]/dt = k_1 [A] [N-R_3] + k_2 [R-Cl] [N-R_3] \quad \text{(A.1)}$$

where

A = azetidinium concentration in the resin

$N-R_3$ = tertiary amine concentration in the resin

$R-Cl$ = chlorohydrin concentrations in the resin (ignoring for the moment any exponential concentration dependencies).

The first term on the right-hand-side of Eq. A.1 gives the rate of disappearance of the azetidinium groups.

The tertiary amine concentration at any time in the reaction is given by

$$[N-R_3] = [N-R_3]_0 - [H^+N-R^3] - \{[R-Cl]_0 - [R-Cl]\} \quad \text{(A.2)}$$

where the second term on the right-hand side of Eq. A.2 accounts for pH effects (protonation of the tertiary amines), and the third term is the amount of resin chlorohydrin groups reacted to form crosslinks with tertiary amines.

Since the observed reaction rate for azetidinium was found to be pseudo first order, it follows that $k_{obs} = k_1 [N-R_3]$. This is only true if the tertiary amine concentration is constant. This, in turn, requires that the third term on the right-hand side of Eq. A.2 be approximately constant over the experimental time scale, which is the expected behavior for a strained azetidinium ring compared to the more stable chlorohydrin moiety. If the reaction is driven at higher temperatures and for longer times, the chlorohydrin reaction can no longer be ignored.

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