The mechanism of wet-strength development in paper: a review

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Not all wet-strength resins operate the same way and, for some resins, the proposed course of reaction has been controversial.

This article reviews the chemistries of wet-strength additives, examines the mechanisms proposed for wet-strength development, and discusses the methods used to deduce these mechanisms. Among the acid-curing resins, urea–formaldehyde resins appear to impart wet strength only by self-crosslinking, while melamine–formaldehyde resins also seem to crosslink the cellulose directly. Among neutral/alkaline-curing resins, azetidinium resins (comprising most polyamide–epichlorohydrin resins) react with cellulose carboxylate groups. At higher addition levels, self-crosslinking becomes more significant. Epoxide resins react analogously and also with the hydroxyl groups of cellulose. Aldehyde resins crosslink cellulose reversibly through hemiacetal bonds, with self-crosslinking through the amide groups also a likely possibility, at least among polyacrylamide–glyoxal resins. For polyethyleneimine, no mechanism suggested so far seems satisfactory.

Background

A wet-strength additive must perform two functions:

- Adhere to the pulp (by adsorption or deposition)
- Form a network that represses swelling of cellulose fibers, thus inhibiting separation of fiber–fiber contacts when paper is rewetted.

Attributes of wet-strength resins

Wet-strength resins share four attributes. They are

1. *Water soluble* (or water dispersible), thus allowing even dispersion and effective distribution on the fibers.
2. *Cationic*, thus facilitating adsorption onto anionic pulp fibers, usually by an ion-exchange mechanism *(1, 2)*.
3. *Polymeric*, with high-molecular-weight polymers being more completely adsorbed and forming stronger bonds.
4. *Reactive*, thus promoting formation of crosslinked networks (with themselves or with cellulose) that resist dissolution in water.

Some electrically neutral, low-molecular-weight materials (formaldehyde, glyoxal) can impart wet strength if they are dried onto pulp. However, these materials cannot be used at the wet end of a paper machine, since they lack a means of retention.

Two principal wet-strength mechanisms

There are two principal mechanisms to explain development of wet strength.

1. *Protection mechanism*. Once an additive is distributed on the fiber (and perhaps diffused into the hemicellulose), the additive crosslinks with itself to form an insoluble network around and through the fiber contacts. When the treated paper is rewetted, this network inhibits fiber separation, thus preserving some fraction of the original dry strength.
2. *Reinforcement mechanism*. The additive reacts with cellulose (or hemicellulose) to form linkages of covalent bonds between cellulose molecules and, presumably, between fibers. These linkages supplement and reinforce the natural hydrogen bonding in the dry sheet. Being covalent, the bonds are not broken by water, and they add their aggregate strength to the structure of wet fibers. It is reasonable to deduce that the reinforcement mechanism is also accompanied by some level of polymer crosslinking, since there is no reason why these polymers cannot self-cure in paper as they do when dried alone.

Importance of resin location on fibers

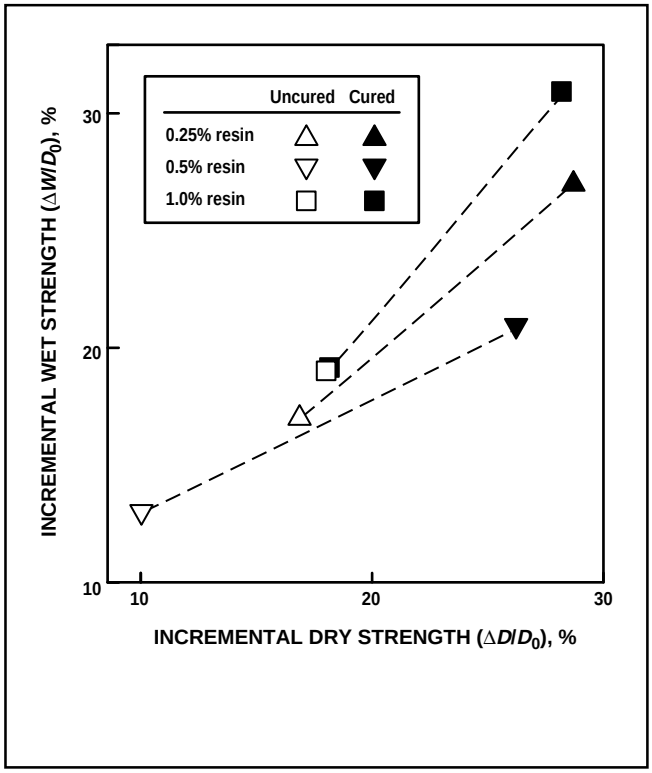
Regardless of how the resin molecules react, they must be located at the weak links of the fiber network if they are to be effective. The Page equation *(3)*

I. Incremental strength effects of polyamide–epichlorohydrin (PAE) resins and carboxymethylcellulose (CMC)

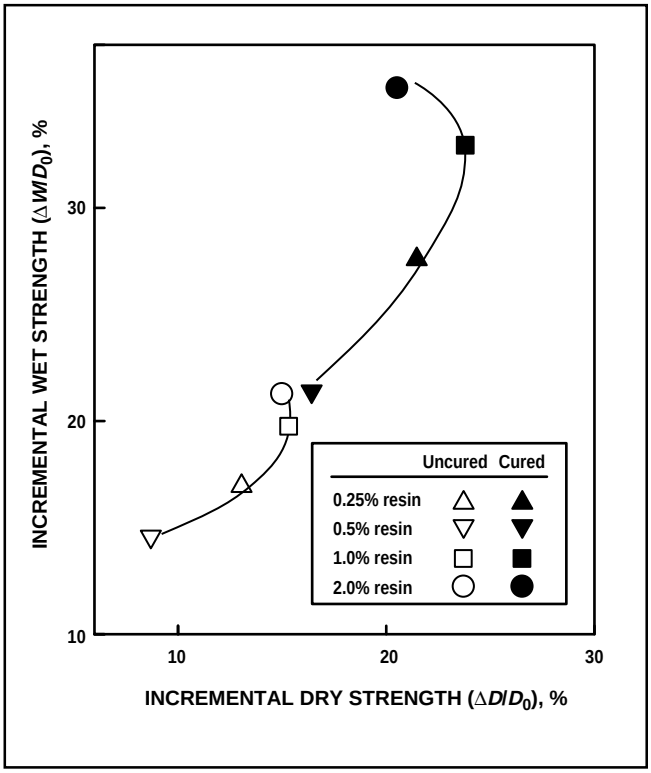
Addition, % of pulp		Breaking length of untreated paper [in brackets] or incremental breaking length of treated paper (no brackets), km				ΔD/ΔW	
		Uncured		Cured			
PAE	CMC	Dry	Wet	Dry	Wet	Uncured	Cured
100% SW bleached kraft [a]							
0	0	[4.33±0.31]	[0.12±0.02]	[4.47±0.25]	[0.14±0.03]	. . .	. . .
1	0	0.74±0.10	0.64±0.12	1.27±0.10	1.06±0.09	1.2	1.2
1	0.5	1.87±0.38	1.32±0.20	2.25±0.39	1.65±0.24	1.4	1.4
50% SW/50% HW bleached kraft [b]							
0	0	[4.08±0.33]	[0.14±0.02]	[4.16±0.31]	[0.16±0.03]	. . .	. . .
1	0	0.48±0.22	0.57±0.08	0.75±0.20	0.83±0.09	0.8	0.9
1	0.5	2.29±0.50	1.33±0.01	2.39±0.29	1.55±0.10	1.7	1.5
50% SW/50% HW bleached kraft [c]							
0	0	[5.03±0.41]	[0.15±0.01]	[4.99±0.37]	[0.17±0.02]	. . .	. . .
0.5	0	0.79±0.07	0.89±0.14	1.21±0.19	1.20±0.26	0.9	1.0
0.5	0.2–0.25	1.45±0.18	1.15±0.09	1.93±0.11	1.42±0.16	1.3	1.4
50% SW/50% HW bleached kraft [d]							
0	0	[4.91±0.32]	[0.13±0.02]	[4.76±0.40]	[0.13±0.01]	. . .	. . .
1	0	0.94±0.28	0.96±0.10	1.53±0.49	1.47±0.26	1.0	1.0
1	0.5	2.1±0.53	1.46±0.09	2.19±0.53	1.80±0.15	1.4	1.2

[a] 675 mL CSF, demineralized water (average of three series)
[b] 500 mL CSF, demineralized water (average of ten series)
[c] 500 mL CSF, hard water (average of four series)
[d] 500 mL CSF, hard water (average of four series)

1. Effect of PAE dosage and heat curing (1 h at 105°C) on incremental wet and dry tensile strengths for bleached kraft pulp (50% HW/50% SW) at 500 mL CSF in water at 100 ppm hardness. Data are averages from 6–8 sets of handsheets at each level of polymer addition.



2. Effect of PAE dosage and heat curing (1 h at 105°C) on incremental wet and dry tensile strengths for bleached kraft pulp (100% SW) at 20°SR freeness in water at 100 ppm hardness. Data are averages from 10–14 sets of handsheets at each level of polymer addition.



$$1/T = 9/8Z + [(12\ A_F\ \rho\ g)/(b\ P\ L\ A_{RB})]$$

shows that breaking length, T, depends on both zero-span tensile strength, Z, and on bond strength, b, (a function of A_{RB}, relative bonded area). However, most wet-strength furnishes are produced using pulps and refining conditions that result in weak fiber–fiber bonds *(4, 5)*. Consequently, strength additives usually are most effective when they enhance fiber–fiber contacts. Migration of cationic polymers from the fiber surface to its interior over prolonged exposure times *(1, 6–9)* can diminish the effectiveness of a wet-strength additive.

Relationship between wet and dry strength

Though wet-strength resins are usually added to impart wet strength, the mechanical strength of the crosslinked network often contributes directly to dry strength. The resin can also have indirect physical and chemical effects on strength. For example, resins that promote flocculation of fines or fibers can change the geometry and bonded area of the fiber network. On the other hand, adsorption of cationic polymers can reduce swelling of suspended fibers *(10, 11)*, thus reducing the bonded area between fibers in the dried sheet. Such loss may partly offset the contributions to strength from formation, fines retention, and the dried resin network.

Tools for investigating wet-strength mechanism

To investigate the interactions of additives with cellulose, one should examine their behavior in cellulose. This is easier said than done. Many wet-end additives are effective at levels of less than 1% based on dry fiber.

Spectroscopy in cellulose

Nitrogen analysis and radiochemical methods can determine the total additive content in paper, but they do not ordinarily distinguish between reacted and unreacted additive. Until the advent of Fourier-transform infrared spectroscopy, most methods of spectroscopy had difficulty quantifying the total of reacted and unreacted additive in the cellulose matrix, let alone distinguishing between them. Mechanistic studies are more difficult yet. When a polymeric additive is used, only a minor fraction of its functional groups may actually have reacted. Moreover, the structures of the main- and side-reaction products may be spectroscopically similar, as well as highly diluted by the cellulose matrix.

Proton *(12–14)*, ^{13}C *(13, 14)*, and ^{15}N *(14)* nuclear magnetic resonance (NMR) spectroscopy can be used to study wet-strength resins. Solid-state samples such as treated cellulose are more difficult to study, and isotopically enriched (^{13}C or ^{15}N) materials are needed for characterization by NMR.

Modeling

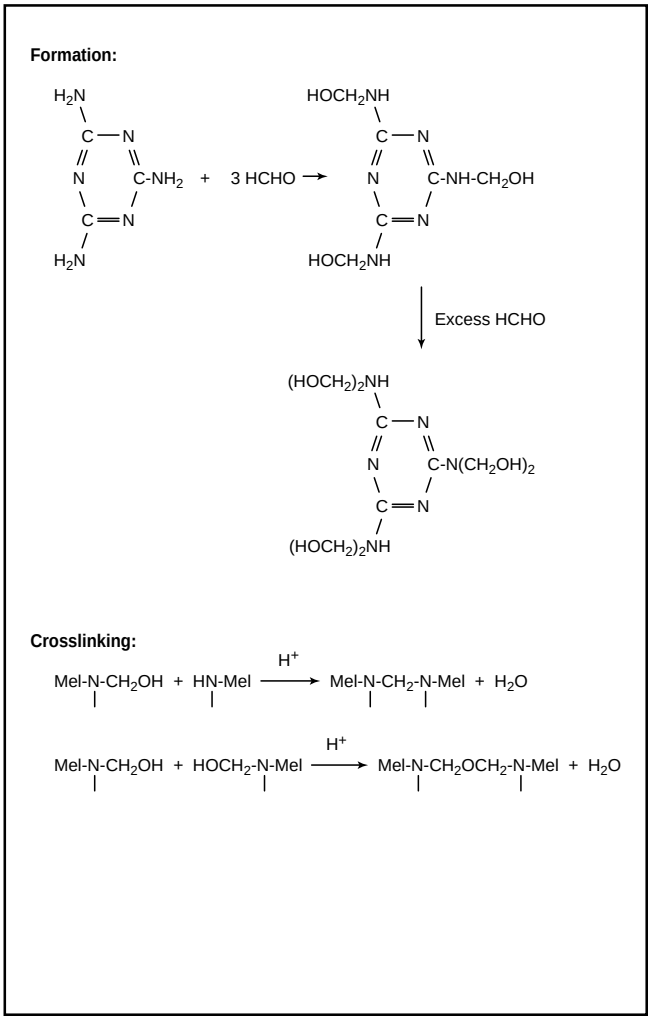
It is common practice to optimize the conditions of a proposed reaction step on a model compound—a less expensive or more accessible compound bearing the same functional groups as a scarce synthetic intermediate. Monomeric reagents can simulate polymeric additives, or monosaccharides (sucrose or methyl α-glucoside) can mimic cellulose *(15–17)*. Successful reaction on a model is considered to be a convincing test of a reaction mechanism.

Modeling is also used to follow the reaction of an additive under modified conditions, where its progress is easier to monitor than in the real-life substrate. Such studies usually involve three or more components, e.g., an additive, cellulose, and water. Often, it is necessary to adjust their ratios to accommodate solubility limitations, analytical sensitivity, time scales, etc. In such cases, the relative importance of competing reactions will differ from the real system.

Fiber physics

Photomicrographs of failure zones in paper samples have provided valuable clues to the kind of bonding between fibers *(17–19)*. When evaluating different additives, it is useful to know whether differences in performance reflect differences in additive retention or in effectiveness at equal retention. Some studies have gone a step further by investigating whether

3. Formation and crosslinking of melamine–formaldehyde resins



II. Dependence of incremental dry/incremental wet strength ratio on pulp refining [a]

	Freeness of untreated pulp, mL CSF			
	Dry			
	642	504	356	205
Dry breaking length, km				
Base sheet	3.73	4.70	5.46	5.83
Incremental dry breaking length from addition of wet-strength resin, km				
0.5% PAE resin [b]	0.89	1.12	0.81	0.97
1.0% PAE resin [b]	1.10	1.31	1.00	1.20
0.5% PMDAAE resin [c]	1.62	1.68	1.49	1.77
1.0% PMDAAE resin [c]	1.87	1.75	1.77	1.86
Wet breaking length, km				
Base sheet	0.14	0.17	0.16	0.19
Incremental wet breaking length from addition of wet-strength resin, km				
0.5% PAE resin [b]	0.90	1.08	1.18	1.25
1.0% PAE resin [b]	0.99	1.26	1.40	1.57
0.5% PMDAAE resin [c]	1.16	1.38	1.57	1.69
1.0% PMDAAE resin [c]	1.36	1.70	1.94	2.21
$\Delta D/\Delta W$				
0.5% PAE [b]	1.0	1.1	0.7	0.8
1.0% PAE [b]	1.1	1.0	0.7	0.8
0.5% PMDAAE [c]	1.4	1.2	1.0	1.0
1.0% PMDAAE [c]	1.4	1.0	0.9	0.8

[a] 50% SW/50% HW bleached kraft pulp in water at 100 ppm Ca hardness and 50 ppm alkalinity. Data are averages from four sets of handsheets (two from each of two batches of beaten pulp); blank controls are averages of six sets of sheets (three from each batch).
[b] Polyamide–epichlorohydrin resin
[c] Poly(methyldiallylamine)–epichlorohydrin resin (base-activated)

III. Effect of increasing resin addition on ratio of incremental dry and wet strengths [*]

	Breaking lengths, km		
	Dry	Wet	$(\Delta)\Delta D/(\Delta)\Delta W$
BL_0 (no resin)	4.35±0.26	0.13±0.028	. . .
$BL_{0.5\%}$ (0.5% PAE resin)	5.55±0.36	1.13±0.10	. . .
$BL_{2.0\%}$ (2% PAE resin)	5.63±0.38	1.34±0.13	. . .
ΔD & ΔW ($BL_{0.5\%}$–BL_0)	1.21±0.25	1.00±0.09	1.2
$\Delta\Delta D$ & $\Delta\Delta W$ ($BL_{2.0\%}$–$BL_{0.5\%}$)	0.075±0.18	0.21±0.07	0.35

[*] 50% SW/50% HW bleached kraft pulp as handsheets at 65 g/m^2 produced from pulp of ca. 500 mL CSF in water at 100 ppm Ca hardness, 50 ppm alkalinity, pH 7.5. Data are averages of 24 pairs of handsheets for each resin condition, with each set from a different batch of beaten pulp.

improved strength is due to an increase in bonded area or to stronger bonding at equal bonded area.

Mechanical-property relationships

In field experience with both strong and weak pulp furnishes, a given dosage of a wet-strength resin often imparts a fairly constant percentage of total wet/total dry strength. This might imply that the crosslinked resin network in the wetted sheet conserves a similar fraction of the original dry strength.

Several investigators have observed that wet-strength additives sometimes increase wet and dry tensile strengths by approximately the same amount *(20–23)*. This has been interpreted in terms of both the protection mechanism (self-crosslinking

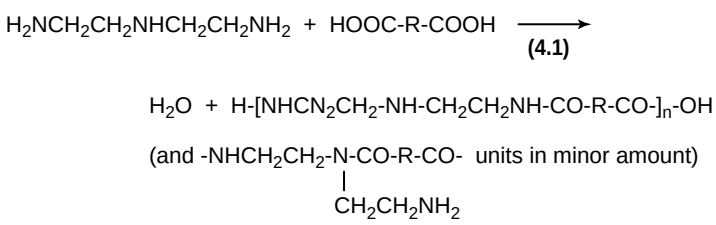
of resin) and the reinforcement mechanism (enhanced fiber–fiber bonding with self-crosslinking).

When based on enough measurements to allow statistical confidence, *differences* in the ratios of dry and wet incremental strengths, $\Delta D/\Delta W$, (all other conditions being constant) can be useful evidence of a difference in mechanisms for two additives. For example, Table I shows data comparing the performance of polyamide–epichlorohydrin (PAE) and carboxymethylcellulose (CMC). However, it is dangerous to draw mechanistic conclusions from *similar* values of $\Delta D/\Delta W$, whether they equal unity or some other chosen value. For example, Table II shows that with a given resin in a given pulp, $\Delta D/\Delta W$ can equal, exceed, or lag unity, depending on the degree of pulp refining *(22)*. This suggests that while dry strength is affected by the number and kind of resin crosslinks, the refining conditions—which affect bonded area, fiber swelling, fines retention, etc.—remain an important factor. Moreover, when a wet-strength paper is oven-cured without changing fiber geometry, the additional strength increments ($\Delta\Delta D$ and $\Delta\Delta W$) can differ from increments off the machine, as seen in Figs. 1 and 2. Finally, simply increasing the amount of resin in the pulp can affect the $\Delta D/\Delta W$ ratio for each resin increment, as seen in Table III. Indeed, at high resin dosage, dry strength can fall as wet strength increases (Fig. 2), possibly because of stress concentration and embrittlement. With so many factors impinging on the resin's effects in paper, an observation of $\Delta D \approx \Delta W$ is neither a constant behavior for a given resin nor the hallmark of a particular mechanism.

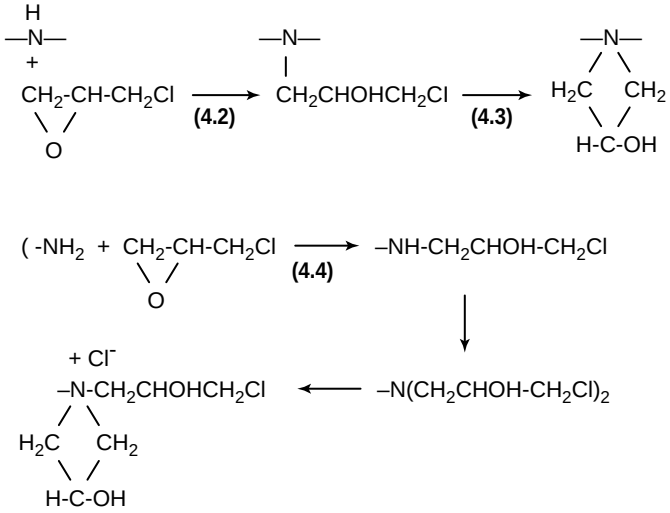
An attempt has been made to factor out the effects of increasing resin retention on the strength increments in increasingly beaten pulps *(22)*. However, the varying trends of ΔD and ΔW could not be easily explained and did not shed light on the mechanism of different resins.

4. Formation and potential crosslinking reactions of PAE resins

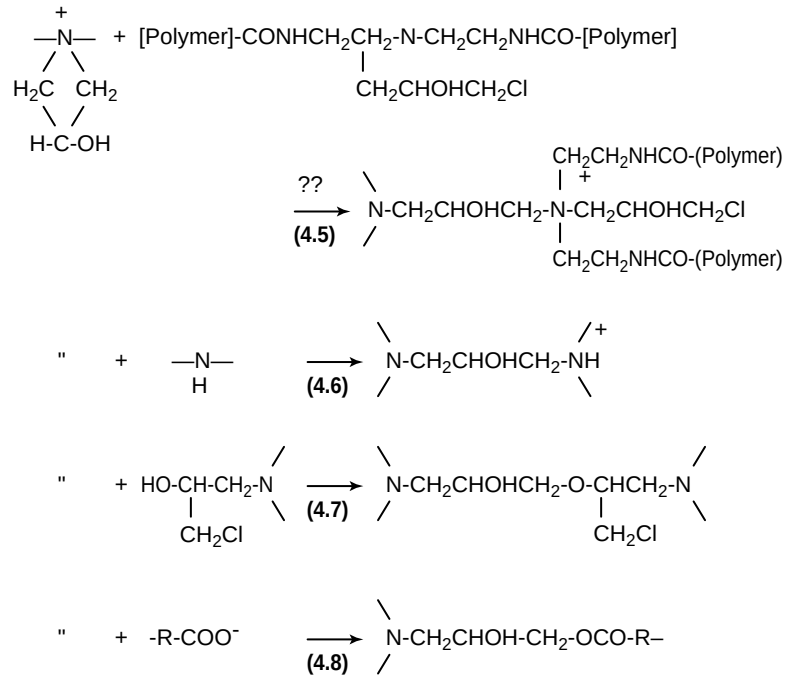
Polyamide formation:



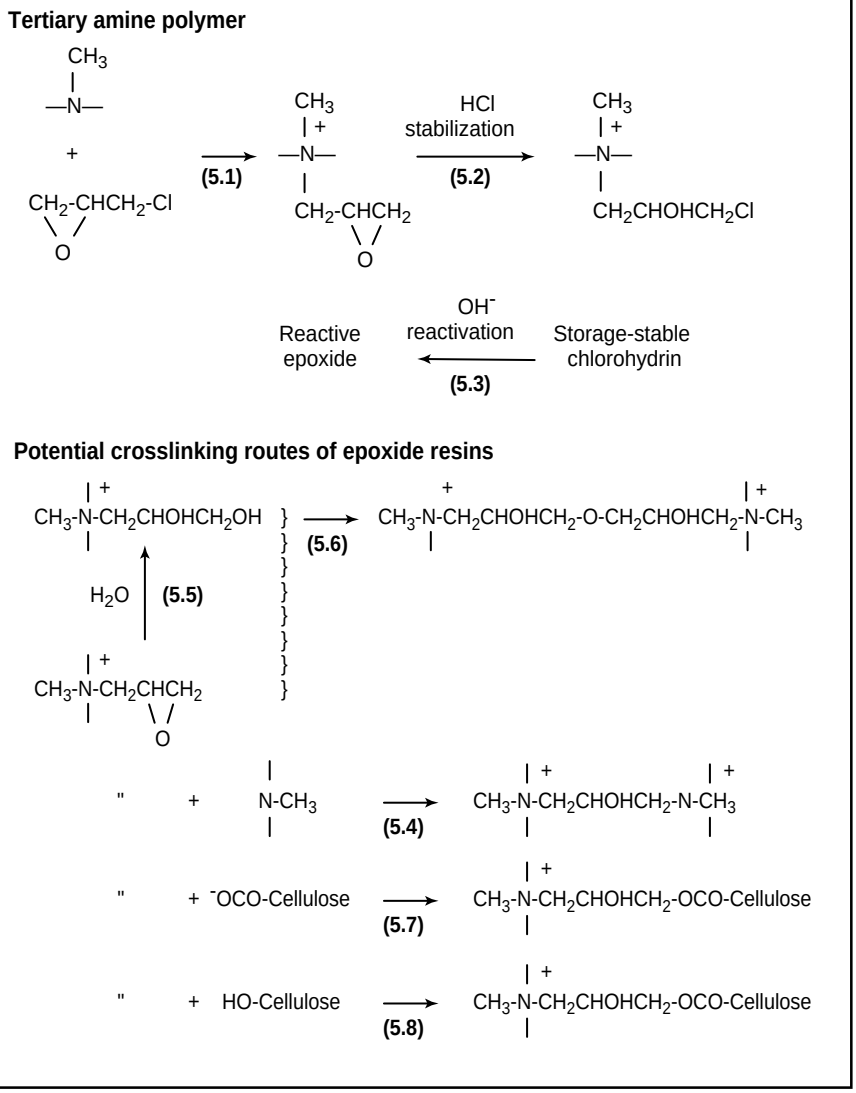
Alkylation by epichlorohydrin and cyclization



Potential crosslinking reactions of azetidinium groups



5. Formation and reactions of quaternary ammonium epoxide resins



Resin chemistry

Acid-curing resins

The earliest cationic wet-strength resins were condensation products of urea and formaldehyde, with polyamine added in small amounts to make them cationic. During synthesis, and again when the resins are dried to an insoluble state, their methylol ($-CH_2OH$) groups are dehydrated to form methylene ($-CH_2-$) and methylene ether ($-CH_2OCH_2-$) bridges between urea units *(24)*. Figure 3 depicts the reactions for melamine–formaldehyde resins, which were developed later. As seen, the methylol groups on trimethylolmelamine (R = H) or hexamethylolmelamine ($R = CH_2OH$) form similar bridges between melamine units *(25–27)* to generate a three-dimensional crosslinked structure.

Neutral/alkaline-curing resins

Azetidinium resins. Azetidinium resins are produced by condensing a polyamine (e.g., diethylenetriamine) with a dibasic acid or its ester to form a poly(amino amide), as seen in Fig. 4, Reaction 4.1. Most of the amine groups of this precursor are secondary (R_2NH), but a minority (<5%) of primary amine (RNH_2) end groups and branches are present, as well as carboxyl end groups. Epichlorohydrin reacts with primary and secondary amine groups to form, respectively, secondary and tertiary aminochlorohydrins (Reactions 4.4 and 4.2). At neutral pH and at temperatures above ambient, the tertiary aminochlorohydrin groups cyclize spontaneously to form 3-hydroxyazetidinium groups (Reaction 4.3). These strained rings confer both reactivity and permanent (pH independent) cationic charge on the resin macromolecule. Some of them, in turn, crosslink the macromolecules concurrently with the alkylation and cyclization reactions during resin manufacture.

In the chemically related polyamine–epichlorohydrin resins, no intermediate polyamide is made. Instead, epichlorohydrin links polyamine units into a long-chain structure, besides alkylating them and cyclizing as in the polyamide resins.

The exact nature of the crosslinks between polymer chains remains unclear. Crosslinks are few compared with other spectroscopically similar sequences in the resin molecule, and it is difficult to detect all of them in the complex ^{13}C-NMR spectra. During resin synthesis, when not all the original secondary amine has been alkylated but some of the early-formed tertiary aminochlorohydrin has cyclized, it seems reasonable that newly formed azetidinium rings can form crosslinks to the remaining secondary amine groups (Reaction 4.6). Molecular-weight distributions measured by size-exclusion chromatography *(13)* suggest that this reaction may be more prominent in low-organic halide (low-AOX) resins made with reduced ratios of epichlorohydrin to amine intermediate *(28–30)*.

The importance of the tertiary amine (from initial alkylation of the original secondary amine) as a crosslinking site (Reaction 4.5) is unclear. The alkylation of unhindered, strongly basic tertiary amines by alkyl halides or epoxides offers a textbook analogy for such a reaction. However, tertiary amine groups of azetidinium resins are only weakly basic. In typical tertiary amines with small unsubstituted alkyl groups, the reaction

$$R_3NH^+ \leftrightarrow R_3N + H^+$$

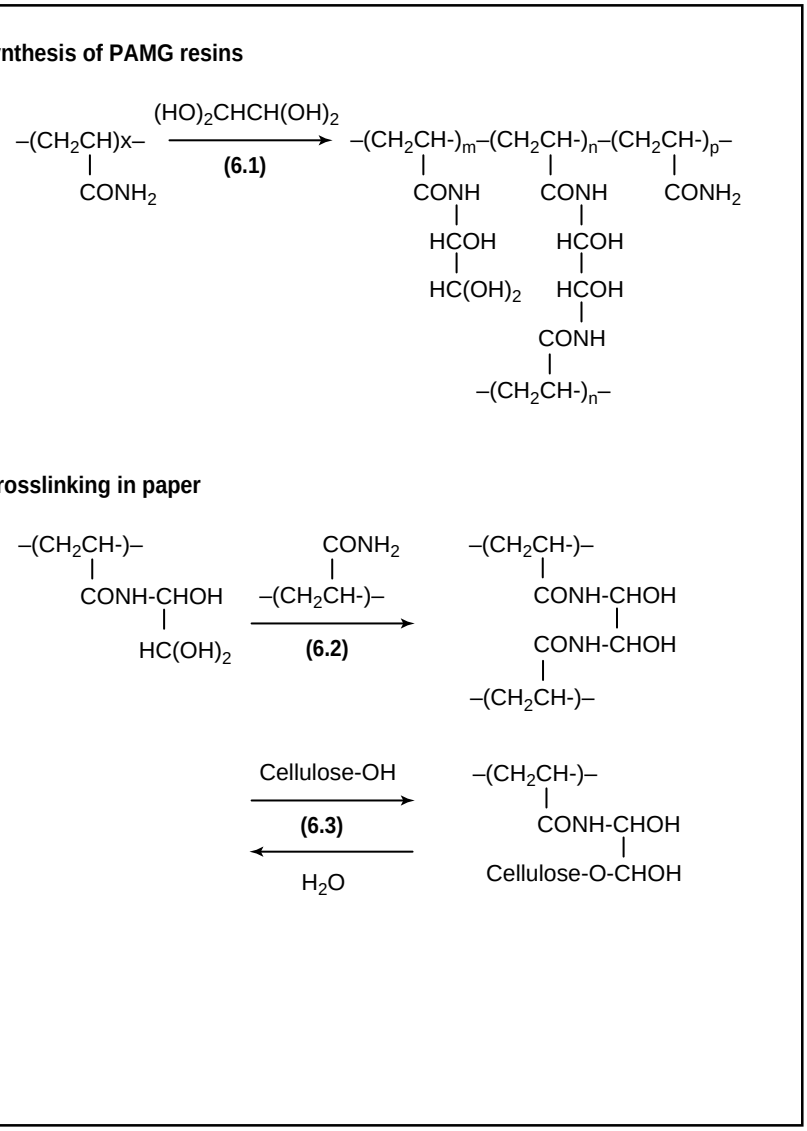
has a dissociation constant of $pK_A \approx 10.5$. In the uncyclized tertiary amine groups of the resin, the combined electron-withdrawing effects of the hydroxyl and amide groups on β-carbons, and the γ-chloride substituent, lower the pK_A to about 5 *(31)*. Steric hindrance from chlorohydroxypropyl and polymeric substituents of the amine groups can further inhibit reaction. This is suggested by the comparative reactivities of diethylenetriamine–adipic polyamide after introducing N-methyl and N-higher alkyl substituents *(14)*.

The azetidinium ring is analogous to an epoxide, toward which alcohols are usually less reactive than amines of normal basicity *(32)*. In competition with the weakly basic tertiary amines in question here, alcohol groups may play a part by default in crosslinking (Reaction 4.7). The reaction of cellulosic carboxyls—discussed later in this article—makes a case for involvement of carboxylate end groups of the prepolymer (Reaction 4.8).

Epoxide resins. In some grades of neutral/alkaline-curing resins, epichlorohydrin reacts with a backbone polymer containing tertiary amine groups rather than secondary amines *(33, 34)*. The resulting reactive functional group is then a quaternary ammonium epoxide, as seen in Fig. 5, Reaction 5.1. Because the epoxide group is more reactive than the 3-hydroxyazetidinium group, resins that bear it will lose effectiveness by hydrolysis on storage unless they are stabilized as the corresponding chlorohydrins (Reaction 5.2). Treating the resin with alkali in dilute solution re-forms the epoxide groups (Reaction 5.3) and restores its full reactivity.

One obvious potential self-crosslinking route (Reaction 5.4) is reaction of an epoxide with a residual tertiary amine group to form a three-carbon crosslink between two quaternary ammonium groups. However, it is uncertain how much the consequent generation of the adjacent second positive charge would inhibit this route. Hydrolysis of one epoxide group to a glycol (Reaction 5.5) followed by reaction with a second epoxide (Reaction 5.6) is possible, but its relative importance is unknown. As with azetidinium resins, it is hard to characterize small numbers of crosslinks among the spectroscopically similar reactive groups on a polymer backbone.

6. Synthesis and crosslinking of polyacrylamide–glyoxal resins



Aldehyde resins

Aldehyde resins encompass two subgroups, both characterized by the formyl or aldehyde (–CH=O) groups as the reactive functional group. The first commercial resin was dialdehyde starch (DAS), used either as a cationic derivative (CDAS) *(35)* or with a cationic retention aid *(36)*. Later, glyoxal-modified polyacrylamide (PAMG) resins were introduced *(37)*. A more recent development is starch derivatives bearing cationic acetal groups, which are hydrolyzed in acidic pulp suspensions to unblock their reactive aldehyde groups *(38)*. All are "temporary" wet-strength additives. Long soaking (>2 h) reduces initial wet strength by one-third to one-half, compared with only 10–20% for formaldehyde-based, polyamide-epi, and polyamine-epi resins.

All aldehyde resins are acid-curing. The dialdehyde polysaccharides lose effectiveness rapidly at system pH above 4.0–4.5. However, PAMG resins maintain their effectiveness up to pH 6, so they can be classified as acid/neutral-curing additives.

Figure 6 summarizes the chemistry of PAMG resins. (Cationic and anionic monomers in the polyacrylamide backbone, which retain the resin on pulp, are not shown.) Addition of

glyoxal to some of the amide groups (Reaction 6.1) introduces reactive functionality to the macromolecule. Some glyoxal units react at both ends (Reaction 6.2), crosslinking the backbone molecules and increasing the resin's molecular weight. The hydrated formyl groups can also react with hydroxylated compounds such as cellulose (Reaction 6.3), losing water to form hemiacetal bonds *(39)*. In DAS, hemiacetal formation between formyl groups and backbone hydroxyls can crosslink the polysaccharide resin, besides bonding it to cellulose.

Investigations of wet-strength mechanism

Formaldehyde-derived resins

Urea–formaldehyde resins. Apparently, wet-strength development by urea–formaldehyde (UF) resins arises only from the restraint of swelling by self-crosslinking. Chemical investigations with cellulose *(20)* or methyl α-glucoside, a cellulose model *(15)*, indicate that UF resins do not react appreciably with these substrates. This conclusion is supported by physical chemistry. The activation energy of wet-strength development on heat curing was independent of the fiber substrate for a variety of pulps, including cellulose and glass fibers *(20)*. Incremental dry strength from UF resins approximately equaled the incremental wet strength in cotton filter paper but not in unbleached kraft pulp, a result that casts doubt on the significance of this ratio in determining wet-strength mechanisms.

Fineman *(40)* found that pulps became unresponsive to UF resin after alkali extraction to remove their hemicellulose. This raises questions about the role of carboxyl groups, which are abundant in hemicellulose. In another study involving cationic UF resin, CMC had no effect on wet or dry strength, even at high dosages that might have interfered with resin retention *(41)*. However, alum in the system may have precipitated the CMC, thus preventing its interaction with resin. Anionic polyacrylamide is more compatible with alum used as a retention aid. However, it likewise had little effect on UF wet strength, and the increase in dry strength was the same as in the alum system *(41)*. By default, the dependence of UF's performance on hemicellulose content seems to rest more on the role of hemicellulose in resin retention—and on UF's physical compatibility with amorphous hemicellulose vs. crystalline cellulose—than it does on chemical reaction with hemicellulose's carboxyl groups.

Melamine-formaldehyde resins. Although the curing reactions of melamine–formaldehyde (MF) resins are similar to those of UF, the former show more signs of reacting with cellulose by a "reinforcement" mechanism. Model experiments with methyl α-glucoside suggest that MF can react with cellulosic hydroxyl groups *(16)*. Photomicrographs show wet-tensile failure occurring in the fiber wall rather than at fiber–fiber contacts *(18)*. Early observations *(21, 22)* of equal incremental wet and dry strenghts with MF resin are inconclusive.

Polyamide–epichlorohydrin resins

Pioneer investigators of polyamide wet-strength resins assumed that the reactive functional groups were aminoepoxides. Later, model-compound studies and NMR investigations revealed the actual identity of the 3-hydroxyazetidinium group *(42, 43)*. Model-compound studies using sucrose *(16)* or methyl glucoside *(17)* indicate that PAE resins do not react readily with cellulose hydroxyl groups. Another study showed that PAE did not insolubilize cellulose toward cupriethylenediamine (CuEn) solvent under normal paper drying conditions, but required oven curing to do so *(44)*, indicating that PAE did not readily form CuEn-stable ether linkages to cellulose hydroxyls.

Another study *(23)* attempted to demonstrate the sole occurrence of self-crosslinking by comparing incremental wet and dry strengths and by measuring the rate of the postulated reaction of the azetidinium group with tertiary aminochlorohydrin (Reaction 4.5). However, the resin concentration (0.4%) in the kinetic study was probably too low for the measured disappearance of azetidinium to represent anything but reactions with solvent—water *(13, 14)*, dimethyl sulfoxide *(45)*, or both. Also, the unnecessary addition of secondary amine (99% of the weakly basic aminochlorohydrin groups would be in amine form at the reported pH 7.95) may have contributed to the rapid initial disappearance of azetidinium. Moreover, the NMR peak assignments were not conventionally calibrated, and there was no spectroscopic evidence of new structures from polymer nucleophiles and azetidinium groups. Finally, hydrogen-bonding effects from added ethanol seem unlikely in the presence of a 2000-fold molar excess of water over ethanol in the reaction mixture. The apparent slowing by ethanol may reflect difficulty measuring reaction rates reproducibly by NMR.

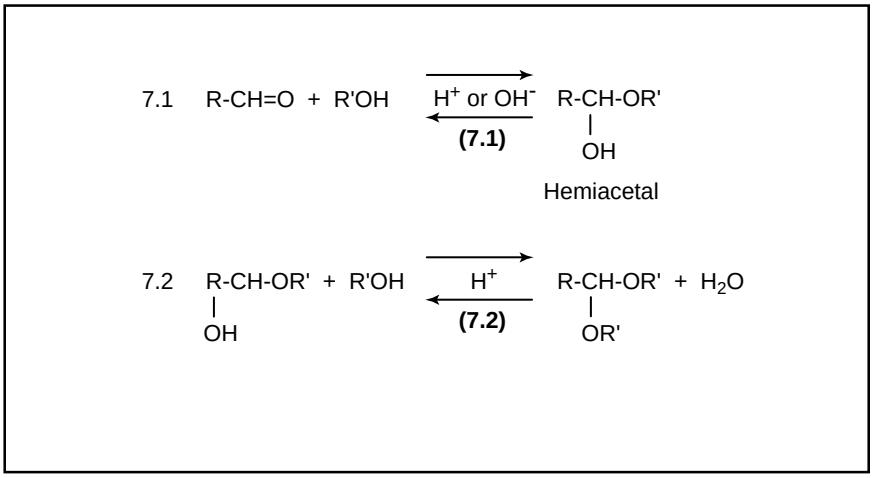
In contrast, direct and indirect evidence supports the reaction of azetidinium resins with the carboxylate groups of pulp. First, the initial 0.1–0.2% (based on dry fiber weight) of retained resin—the amount needed to titrate pulp carboxyls and adjust the pulp to zero electrophoretic mobility—yields substantially more wet strength than addition of more resin, on a per-unit-resin-retained basis *(44)*. This heightened response is modeled by the increased effectiveness of PAE in the presence of CMC or other carboxyl-bearing dry-strength polymers (Table I).

This indirect evidence is supported by results of an investigation of PAE in carboxylated pulp *(46)*. This study showed that PAE increased wet strength at equal bonded area between fibers. It also showed direct spectroscopic evidence for the reaction of azetidinium resins with pulp carboxylate to form ester groups. Another investigation *(19)* of PAE–CMC combinations showed that at sufficiently high dosages, the fiber–fiber bonds are so strengthened that failure occurs in the fiber walls. Studies of electrophoretic mobility using polyethyleneimine (PEI) *(7)* and electron microscopy using PAE *(1, 17)* provide evidence that cationic PAE can migrate beneath the surface of cellulose fibers. However, the electron microscopy of stained fibers did not unequivocally measure the thickness of the resin layer on the surface *(1, 17)*.

One apparently inconsistent piece of experimental evidence is: If PAE resins crosslink cellulose through its carboxyl groups, why does the treated paper remain soluble in CuEn? The clue

is that dried PAE resin itself, though water-insoluble, is also CuEn-soluble *(44)*. Apparently, the amine solvent cleaves the amide groups in the resin's backbone polymer. Primary amines cleave esters at room temperature to form amides and alcohols, so it seems likely that the En component of CuEn solvent likewise cleaves the ester crosslinks in papers made with PAE.

7. Hemiacetal and acetal formation



Epoxide resins

In general, epoxide resins react qualitatively like azetidinium resins but quantitatively faster. In many paper grades, they impart higher wet strength (after curing or aging), and they develop a larger fraction of that higher final strength off the machine. They also react faster with water (in their epoxide form). In the one known comparative study of their mechanism, an epoxide resin (with an amine-resistant backbone) partly insolubilized cellulose toward CuEn, unlike an azetidinium resin with a similar backbone *(44)*. This suggests that epoxide resins react not only with cellulose carboxyl groups (Reaction 5.7), but also with hydroxyl groups (Reaction 5.8) to form ether groups, which are inert to aminolysis.

Aldehyde resins

Aldehyde resins (including aldehyde derivatives of polysaccharides and glyoxalated polyacrylamides) are believed to react with cellulose hydroxyl groups to form hemiacetal linkages *(39)*. At first glance, the pH dependence of these resins does not agree with textbook descriptions of aldehyde chemistry, given in Fig. 7. The equilibrium formation of an aldehyde with an alcohol to form a hemiacetal (Reaction 7.1) is catalyzed by either acid or base. However, wet-strength development by these resins, especially DAS, is only acid-catalyzed. Moreover, alkali rapidly degrades the wet strength imparted by these resins. If alkali catalyzes the reverse reaction, why does it not catalyze the forward reaction? One possible explanation is that of "full" acetal formation (Reaction 7.2), since only acids can catalyze the reaction of a hemiacetal with a second equivalent of an alcohol to form an acetal. However, acetals are stable to base, so any significant acetal formation should impart alkali-proof wet strength.

Strength imparted by aldehyde resins probably develops by way of hemiacetal formation. In a reaction catalyzed by either acid or base, the point of minimum rate (where changing pH in either direction accelerates one route more than it slows the other) need not be at pH 7. It is possible that the base-catalyzed route requires a pH high enough to degrade the additive by other side reactions of the formyl group, or to alter the behavior of the cellulose. If this is the case, then only the acid-catalyzed hemiacetal formation would be observed within the range of pH conditions usual in papermaking. Conversely, alkali would be used only under repulping conditions, where dilution favors hydrolysis of the hemiacetal.

As the pH of a papermaking system increases above 4.0–4.5, polyacrylamide–glyoxal resins maintain more of their effectiveness than do polysaccharides (DAS). This may occur because crosslinking of amide groups by glyoxal becomes faster as pH rises in the range 7–9 *(41)*. It seems plausible that as acid-catalyzed crosslinking of cellulose by the aldehyde becomes slower with rising pH, it is supplemented by base-catalyzed self-crosslinking of the additive. Under repulping conditions with excess water present, both reactions could be reversed with alkali catalysis, and hemiacetal formation could also be reversed with acid.

Polyethyleneimine and chitosan

This pair of polymers challenges our understanding of wet-strength mechanism, since both impart substantial wet strength to paper without bearing any obviously reactive crosslinking groups. A number of explanations have been offered for the wet-strength effects of PEI, none of them completely convincing.

One explanation refers to the multiple ionic bonds by the protonated amine groups of PEI, so strong or so numerous that water cannot break all of them at once *(47–49)*. However, other highly cationic nonreactive polymers [poly(dimethyldiallylammonium chloride)] fail to impart wet strength *(41)*, so multiple ionic bonding by itself does not explain the matter.

Similarly one can invoke a multiplicity of hydrogen bonds, again so numerous that water does not cleave them all at once. Again, if this were true, many other strongly hydrogen-bonding polymers [polyacrylamide and poly(vinyl alcohol)] would also impart substantial wet strength, but they do not *(41)*.

One could also postulate some sort of sterically favored complex of the wet-strength agent with cellulose. Intuitively, this sounds more likely for chitosan than for normal PEI, whose irregular, highly branched structure seems ill-suited to conform repeatedly to the structure of a cellulose macromol-

ecule. Moreover, experimental linear PEI, which might conform better, imparts much less wet strength than the conventional branched polymer *(41)*.

The so-called "jack-in-the-box" mechanism *(50, 51)* postulates that PEI diffuses into microcracks and pores in the fiber surface, where it becomes stuck because its molecular volume expands with pH changes. This mechanism neatly and plausibly explains why PEI, once sorbed on (or in) a fiber, is difficult to remove. It is less obvious, however, why the fiber–fiber contacts resist dissociation on wetting just because the fibers contain trapped PEI.

Finally, another potential explanation rests on amide formation between amine groups of the additive and carboxylate groups of the pulp *(52)*. However, this condensation reaction usually requires substantially higher temperatures than those achieved on normal paper dryers. The observed amide formation warrants confirmation before this explanation can be entirely satisfying.

Directions for research

A review of wet-strength mechanisms suggests several directions for future research.

- As spectroscopic techniques become more refined, they should be applied to the structure of crosslinks in PAE and epoxide resins.
- More remains to be learned about additives under conditions that favor intrafiber reinforcement vs. interfiber bonding and from tests (e.g., compression or crush strength) that depend on other modes of failure.
- The substantial wet strength from nonreactive amine polymers (PEI and chitosan) remains to be convincingly explained.

Summary

Urea–formaldehyde resins impart wet strength primarily by self-crosslinking, i.e., by protecting existing fiber bonds. In contrast, melamine–formaldehyde resins appear to operate by also reacting with cellulose.

Among the neutral/alkaline-curing resins, PAE resins react with the carboxylate groups of hemicellulose as well as by self-crosslinking (especially at higher resin dosages).

The pH dependence of aldehyde resins, and the reversibility of their wet strength, are consistent with their reaction with cellulosic hydroxyl groups to form hemiacetals. The pH behavior of polyacrylamide–glyoxal resins suggests the additional occurrence of amide-to-amide self-crosslinking as well.

The mechanism of wet-strength development by nonreactive amine polymers remains obscure. TJ

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