

Some properties of newsprint impregnated with polyvinylamine

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ABSTRACT: We measured wet-strength and dry-strength properties of newsprint impregnated with polymers in the polyvinylamine family. Polyvinylamine is a recently commercialized polymer with the potential to increase the tolerance of wood-containing papers to water-based printing processes. Poly(*N*-vinylformamide) (PNVF), the precursor to polyvinylamine (PVAm), increased dry strength but not wet strength. Both PVAm and partially converted PNVF-co-PVAm copolymers increased both wet strength and dry strength dramatically. Over the range of 56% to 100% conversion of PNVF to PVAm, there was little difference in the wet strength of the resulting paper. The wet strength of PVAm-impregnated newsprint was a little higher at pH 10 than at lower pH values. Drying at 120°C gave only slightly higher wet strength than did drying at room temperature.

Application: This paper assesses some of the performance characteristics of a newly available surface-strengthening polymer for newsprint.

Mechanical pulp is a relatively inexpensive and environmentally friendly source of papermaking fibers. However, its brightness, color, light sensitivity, and printing characteristics limit its use in high-performance printing papers. Based on the scientific achievements of the Canadian Mechanical Woodpulp Network, commercial solutions are now available for both the yellowing problem and the brightness problem [1, 2]. However, the problems of printing characteristics have not yet been overcome. Printing operations that involve exposing the sheet to moisture can be particularly awkward for wood-containing sheets. Fiber rising and linting are cited as common symptoms of a weak, moisture-sensitive paper surface in offset printing [3]. Presumably, water from the nonimage area on the blanket, along with water emulsified in the ink, enter the paper and weaken fiber-fiber bonds. However, data relating linting to moisture exposure seem to be lacking [4].

Coating is the conventional way to improve the printing properties of wood-containing papers. Lightweight coated grades, for example, are made in an off-machine process in which a coating of pigment and latex are calendered to give an improved printing surface. On-machine coating with polymers, with or without pigments, is a less costly approach to improving surface strength. Conventional size presses, metered film coaters [5], curtain coaters, and spraying have been employed to coat paper with starch and other polymers. It seems rea-

sonable to predict that there will be growth in the use of on-machine coating technologies for the surface treatment of wood-containing papers.

In this work we consider polyvinylamine (PVAm) as a potential polymer for strengthening the surface of newsprint and related paper grades. Although PVAm has been described for decades in the polymer literature, it has recently attracted interest as a paper additive because of the discovery that PVAm can be efficiently manufactured from the hydrolysis of poly(*N*-vinylformamide) PNVF (Fig. 1). PVAm and partially hydrolyzed PNVF were commercially available to the paper industry for the first time in 2001–2002.

In addition to the patent literature, there have been a few reports of polyvinylamine applications in paper. Geffroy *et al.* studied the kinetics of PVAm adsorption onto cellulose [6]. Tanaka's group has investigated PVAm as a flocculant and size fixing agent [7]. Wågberg and Asell compared polyvinylamine to other cationic polymers as agents for fixing dissolved and colloidal substances [8].

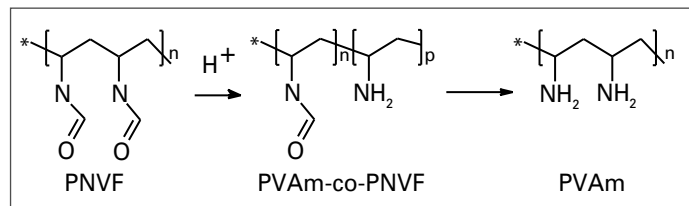
Polyvinylamine is a linear hydrocarbon chain with pendent, primary amine groups on alternating carbons. Some of the relevant chemical reactions of primary amines are summarized in Fig. 2. First, primary amines are strong bases that can be protonated by water to give positively charged ammonium groups (Fig. 2A). In the case of small molecules, the primary amine groups are strongly basic. In an aqueous solution of methy-

lamine, for example, roughly half of the amine groups are charged (protonated) at pH 10.6. Under normal papermaking conditions (pH 4.5–7), essentially all the ethylamine in water is positively charged.

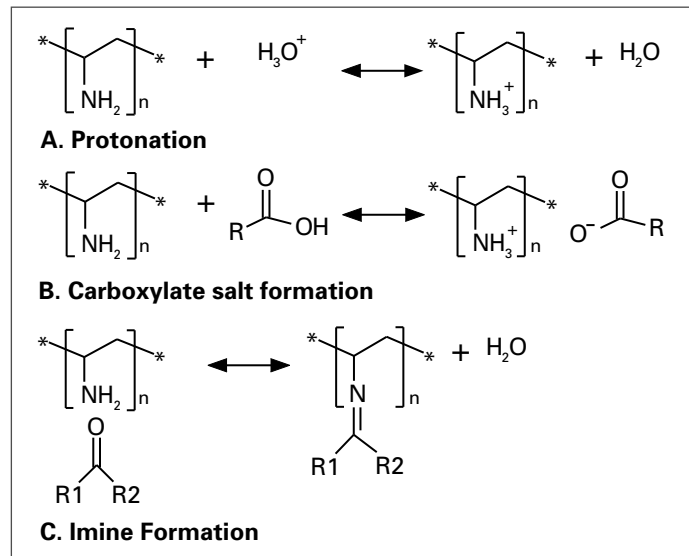
Because of nearest neighbor effects, polymers are weaker bases. Published titration results indicate that at pH 7 roughly half of the amine groups on polyvinylamine are not charged. Indeed, pH values less than 1 are required to fully protonate the PVAm. If it is assumed that under normal papermaking conditions the degree of protonation is 0.5, then the equivalent weight (charge content) is 8.2 meq/g for the hydrochloride salt of PVAm. By comparison, the commonly used poly(diallyldimethylammonium chloride) has a lower charge content of 6.2 meq/g. Because of its high cationic charge content, polyvinylamine readily adsorbs onto fibers [6, 9], coating fiber surfaces with both cationic protonated and free ammonium groups.

Primary amine groups will react with aldehydes and ketones to form imines (Fig. 2B). For example, Neogl and Jenson describe a process for increasing the aldehyde content on fibers to encourage imine bond formation [10]. Imines formed from low-molecular-weight alkyl aldehydes and ketones readily hydrolyze in water. There is no published direct evidence of imine formation when paper is treated with polyamines.

Finally, amines can form ammonium carboxylates (Fig. 2B), which should have a significant effect in papermaking because of the carboxyl groups present



1. The hydrolysis of PNVF to give PVAm and copolymers.



2. Some amine chemistry.

in mechanical pulps. In water the electrostatic interaction between positively charged polymers and negatively charged fibers causes polymer to adsorb onto the fibers in an ion-exchange process.

Here, we report on the wet- and dry-strength properties of newsprint impregnated with polyvinylamine. Polymer loading, the degree of PNVF hydrolysis, the treatment pH, and the drying conditions are considered.

EXPERIMENTAL PROCEDURES

Materials

Analytical-grade solvents were used as received. Millipore-Q® water was used for all experiments. Solutions of 36.5% HCl (BDH) and KOH (BDH) were used to adjust pH. We purified 98% *N*-vinylformamide (NVF) from Aldrich by distilling it under vacuum at 70°C to give a clear, colorless liquid. Sorbitan monostearate (Span 60, Aldrich) was used as supplied, and the initiator, 2,2'-azo-bis-isobutyronitrile (ABIN), was recrystallized in ethanol before use. For testing paper strength, we used newsprint with a high content of recycled paper and a basis weight of 45.46 (0.24 g/m², a gift from Abitibi-Consolidated Thorold Mill.

Synthesis of poly(*N*-vinylformamide)

Water-soluble poly(*N*-vinylformamide) (PNVF) was prepared by polymerizing NVF using 2,2'-azo-bis-isobutyronitrile (ABIN), a free radical polymerization initiator [11]. This precipitation polymerization was carried out in a three-necked, 500 mL reactor equipped with an impeller stirrer set at 750 rpm and a nitrogen purge. The reactor was placed in a water bath (NESLAB) controlled at 62°C. Following the work of Gu *et al.* [12], we added 30.8 g of NVF, 3.00 g of sorbitan monostearate (Span 60),

and 190 g of toluene in sequence. When temperature equilibration was reached, we injected ABIN (0.031 g in 10 g toluene) into the reaction mixture.

The stirred mixture was polymerized under nitrogen for 8 h. The white precipitate was washed in methanol six times by filtration to remove the solvent, toluene, and unreacted monomer. The resulting polymer, PNVF, was vacuum dried at 20°C for 48 h. Three batches of PNVF were prepared and combined to give us the PVNF sample (MW=5 × 10⁵ Dalton) we used in our experiments.

Hydrolysis of PNVF

PNVF was hydrolyzed to give PVAm and PNVF-co-PVAm copolymers (Fig. 1). Three samples of 8.00 g of the 10 wt% aqueous PNVF were prepared and were mixed with 15.3 g (1.30 molar ratio) of 36.5% aqueous HCl. These mixtures were heated to 75°C. The hydrolysis times were 30 min, 1 h, and 70 h. **Table I** summarizes the resulting charge contents. The hydrolysis products were precipitated with methanol and were vacuum-dried for two days.

Polymer characterization

We obtained the molecular weight distribution of PNVF by gel permeation chromatography (GPC) using the Waters 2410 Differential Refractive Index Detector and the Waters 2690 Separations Module with three Waters Ultrahydrogel™ linear columns. The system was calibrated with polyacrylamide, with 0.05*N* NaNO₃ as solvent and a flow rate of 0.8 cm³/min at 30°C.

The degree of hydrolysis of PNVF was determined from the ¹H spectra recorded from a Bruker AC 200 NMR Spectrometer. ¹H chemical shifts were adjusted relative to the D₂O peak at 4.65 ppm. We checked the NMR results with polyelectrolyte titrations conducted with a Rank Brothers Charge Analyzer II fitted with a Metrohm 665 Dosimat automatic buret. In a typical experiment, 200 mL of 2000 ppm polymer solution at pH 4.5 was added to the titration vessel containing the streaming potential probe. Excess 0.001*M* anionic potassium salt of polyvinylsulfate was added. After a few minutes of mixing, the uncomplexed polyvinylsulfate was back-titrated with 0.001*M* cationic polybrene. The degree of PNVF hydrolysis was calculated from the equivalent weight. Reported results were based on the average of three measurements.

Paper sample preparation and testing

Newsprint sheets, 24.5 cm × 16.7 cm, conditioned at 23±0.5°C and 50±1.0% RH for at least one day, were weighed and placed in a Pyrex dish (11 in. × 7 in. × 1.5 in.). Polymer solution (7.5 g in 200 mL) was poured onto the sheets, which soaked for 30 min. Excess polymer solution was decanted, and the wet sheets were weighed. We calculated the polymer content from the mass balance. The polymer concentrations in the impregnation solutions, expressed as a mass fraction, ranged from 0% to 4%. The pH values of the impregnation solutions were usually adjusted to pH 7.

In a few cases, the wet sheets were tested immediately after impregnation. Results from these samples are designated WND (for "with no drying"). Mainly the impregnated sheets were dried at ambient conditions, while being restrained in hand-sheet rings (with these samples designated RTD for "room temperature drying"), or the impregnated sheets were dried for 15 min at 120°C (designated HTD for "high temperature drying") in a LABTECH OMRON speed dryer.

We measured dry strength according to TAPPI methods. Tensile measurements were made with an Instron Model 4411. The gauge length of the specimen between the clamps was set at 100 mm. For each experimental condition, we tested 14 samples for dry strength and 6 specimens for wet strength. We used 50 N load cells for wet strength measurements and 500 N load cells for dry strength. The strain rate was 10 mm/min for all tensile measurements. The internal bond strength values were measured with a Huygen internal bond tester, Model 1314.

We measured wet tensile strength with sheets rewetted in water and soaked for 30 min. The pH of the rewetting solution was adjusted to equal the corresponding impregnation solution.

RESULTS

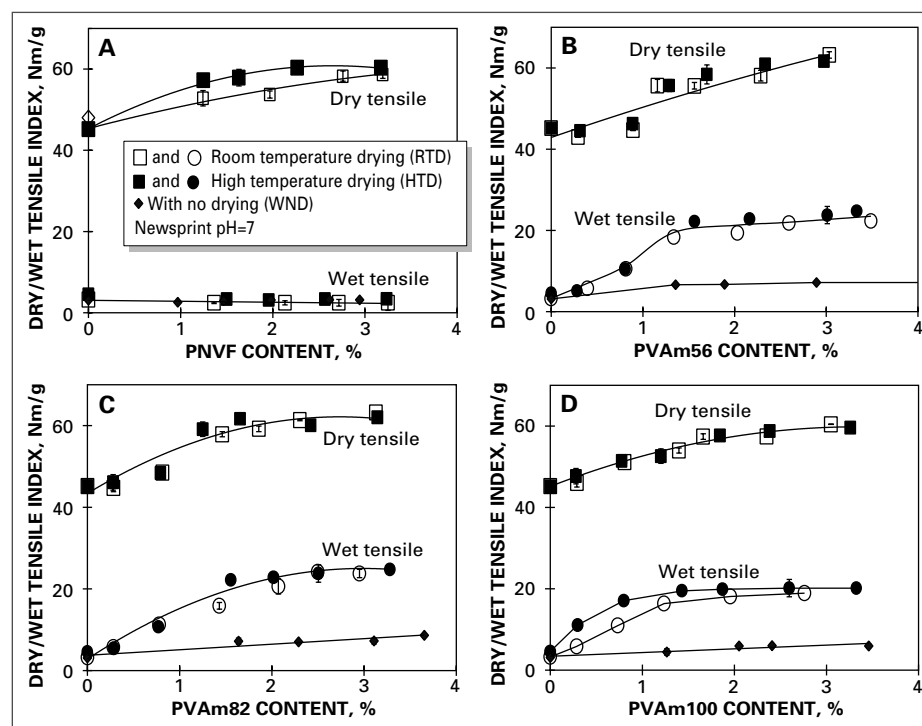
Newsprint sheets were immersed in polymer solutions and were tested for wet and dry strength. Figure 3a shows tensile strength results for the unhydrolyzed PNVF. The dry strength increased with polymer addition, and the strength was slightly higher for sheets dried at 120°C than for those dried at room temperature. The dry strength of sheets treated with the PVAm polymers (Fig. 3b, c, d) were not sensitive to drying conditions. This observation contrasts the recent report of Rathi and Biermann, who showed that for kraft pulp hand-sheets wet-end treated with polyallylamine, the dry strength of the paper sample dried at high temperature increased by a factor of 1.17 over the dry strength reached by drying the sample at low temperature [13].

Comparing the untreated paper with the control experiment, which was paper impregnated with water, we found that the impregnation process lowered the tensile strength by about 7%, with about 1% polymer required to obtain the starting dry tensile strength. Finally, PNVF showed no activity as a wet strength resin.

The impregnation process caused a significant decrease in sheet density. The initial newsprint density was 686 kg/m³, whereas after impregnation and drying the densities were in the range of 420–468 kg/m³ [14]. Drying temperature had no influence on sheet density.

DESIGNATION	REACTION TIME, h	HYDROLYSIS DEGREE FROM NMR, %	CHARGE DENSITY FROM CHARGE TITRATION, Meq/g	HYDROLYSIS DEGREE FROM CHARGE TITRATION, %
PNVF	0.0	0.0	—	—
PVAm 56%	0.5	43.5	7.12	56.3
PVAm 82%	1.0	77.1	10.4	82.0
PVAm 100%	70.0	100.0	12.7	100.0

1. Hydrolysis times and resulting polymer properties.



3. The comparison of dry and wet tensile strengths for PNVF at pH 7. The error bars show the standard deviations of the mean tensile strengths.

PNVF was hydrolyzed to give 56%, 82%, and 100% conversion to polyvinylamine. The tensile strength results (Figs. 3B, C, D) showed that both dry strength and wet strength improved with polymer addition. The never-dried impregnated sheets all gave low indices for wet tensile strength. Thus, drying is an important step for the wet strengthening process with PVAm and its copolymers. On the other hand, the drying temperature did not seem to be very important—higher temperature drying gave only slightly higher wet strength.

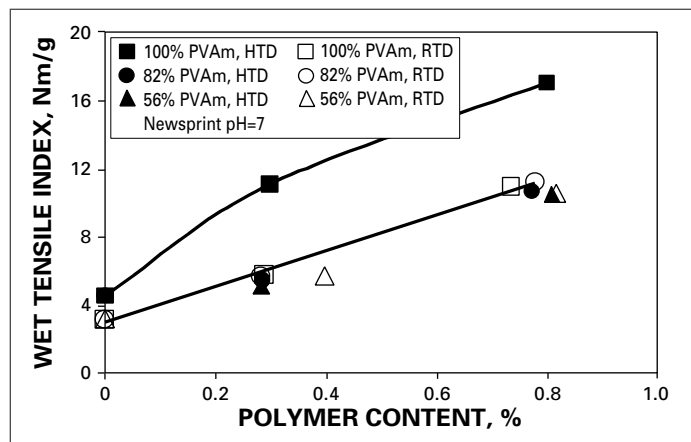
Wet strength results in Figs. 3B, C, and D also reveal that in the range of 56–100%, wet strengthening was not sensitive to the degree of hydrolysis. Furthermore, the slopes of the curves were similar for wet and dry strength.

Figure 4 compares the wet strength results for the three polymers containing

amine at low dosage. The 100% hydrolyzed PVAm dried at high temperature gave slightly higher strength than did the other five samples, which fell on the same line.

Figure 5 shows the influence of rewetting time on the wet tensile strength of paper impregnated with polyvinylamine. The dramatic capability of PVAm (56%) to increase wet strength did not significantly decrease with rewetting time. Thus, room temperature soaking at pH 7 did not destroy PVAm-induced bonds in the one-hour time frame, which suggests a permanent improvement in wet strength. PNVF did not improve wet strength and therefore was not sensitive to rewetting time.

Figure 6 shows the internal bond strength as a function of polymer content. All the polymers increased internal bond strength—the maximum increase



4. The influence of drying methods and hydrolysis degree on wet tensile strength.

was from 200 J/m² without polymer to 500 J/m² with 3% polymer. Above 2% the PNVF was less effective than were the amine-containing polymers. As with the tensile strength results, room temperature drying gave slightly lower internal bond strength than did drying at higher temperature, as the figure illustrates.

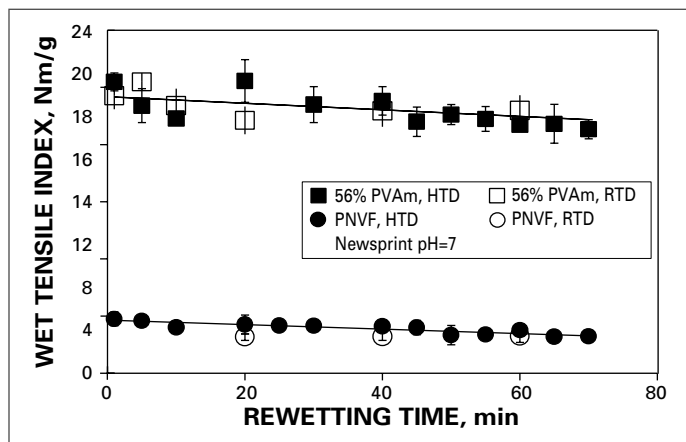
Wet strength was measured as a function of impregnation pH, and the results are summarized in Fig. 7. The rewetting pH values were the same as the corresponding impregnation pH values. There were pH effects. The highest wet strength occurred at pH 10, whereas the wet strength at pH 7 was only slightly higher than that obtained at pH 3.5. As before, drying temperature effects were minor, with a slight advantage to high temperature drying.

DISCUSSION

One of our goals in this research was to determine the factors that influence the ability of polyvinylamine to improve surface strength, particularly in the presence of water. However, we did not measure surface strength. Instead, we used total-sheet wet strength as an indicator of the strength of a wet paper surface. Although surface strength is important, the methods to measure it are not well developed. Wax pick and tape peel [15] give a measure of dry surface strength, although these methods are not generally employed for damp or wet paper surfaces. The IGT is perhaps the most widely used test method in the paper industry [16]. This test attempts to mimic the tack forces experienced by a paper surface during printing.

Adding polymers that enhance wet strength is not the only approach to increasing the tolerance of paper surfaces to water. Sizing is the standard approach to limiting water uptake during printing. Although many mechanical pulps are partially sized naturally, an effective strategy for surface strengthening may be to use a combination of size and wet-strength resins. However, we did not consider sizing in this work.

When the goal is to improve surface strength, it seems logical to concentrate strength-enhancing polymer at the paper surface, perhaps by coating from a viscous solution. In this study, we treated the entire sheet by impregnation and then measured the overall mechanical properties to get an idea of the potential for the polymers to improve surface strength. However, the impregnation procedure caused the paper to swell and weaken. Also, the fact that the entire sheet was treated meant that high polymer loadings were required. On the other hand, in a com-



5. The influence of rewetting time on wet tensile strength. The small effect indicates a permanent type of wet strengthening.

mercial coating application, the PVAm could be concentrated at the surface, where it would have the greatest effect.

Research papers describing wet-strength resins usually discuss the mechanism of wet strengthening because this mechanism is a fascinating scientific problem. In the case of polyvinylamine, the addition of a totally water-soluble polymer to a hydrophilic paper sample increases the wet strength by a factor of ten, although the reasons for this increase are not obvious. Excellent review articles have been published [17, 18], and this body of work leads to two generally accepted concepts of wet strengthening.

First, most wet-strength resins form strong covalent bonds when dried. Second, some wet-strength resins predominately form covalent bonds with themselves, a process called "homo-crosslinking," whereas other resin types react predominately with fibers, in "co-crosslinking." For example, PAE resins are believed to react predominately with themselves [19], whereas starch aldehydes can form hemiacetal bonds either with other starch molecules (i.e., homo-crosslinking) or with the fibers (co-crosslinking). In the case of polyamines, the issue of covalent bond formation is unresolved. Imine formation (Reaction C in Fig. 2) may occur, although there is no direct evidence of this in the relevant literature. Both in our work and in Rath's polyallylamine work [13], high-temperature drying gave slightly higher wet strength. This result gives some support to the supposition that covalent bonds are being formed through a chemical reaction. If polyvinylamine does form chemical bonds, then these bonds will probably be the co-crosslinking type, since amine-amine reactions seem most unlikely. Indeed, films cast from aqueous PVAm solutions dried at 105°C readily redissolved in the presence of water, indicating no homo-crosslink formation.

There is little doubt that electrostatic interactions are behind the adsorption of polyvinylamine on anionic pulp fibers. Similar interactions result in complex formation with soluble anionic polymers [20]. On the other hand, it does not necessarily follow that ionic bonds contribute to wet strength.

From a polymer chemistry perspective, the closest analogues of PVAm that have been studied as wet strengthening polymers are polyethyleneimine (PEI) and polyallylamine. PEI is an amine-containing polymer which has found widespread use. Unlike PVAm, PEI is branched with secondary and tertiary

amines as well as primary amine groups. Nevertheless, the wet-strengthening mechanism of PEI may be similar to that of PVAm.

In a study published in 1951 on the wet strengthening mechanisms of PEI [21], Trout showed that ion exchange was the driving force for adsorption. He also measured the sodium ions released when protonated amine groups on PEI formed salts with the carboxylate groups bound to fibers. Furthermore, he showed that the magnitude of wet strength improvement increased with the strength of PEI adsorption measured as released counter ions. Finally, he showed that the presence of formaldehyde gave internal crosslinking of the PEI, which further increased wet strength. Interestingly, there was no evidence for increased wet web strength. These insights were remarkable in light of the tools available in 1951. Sarkanen and coworkers verified Trout's mechanistic conclusions 15 years later [22].

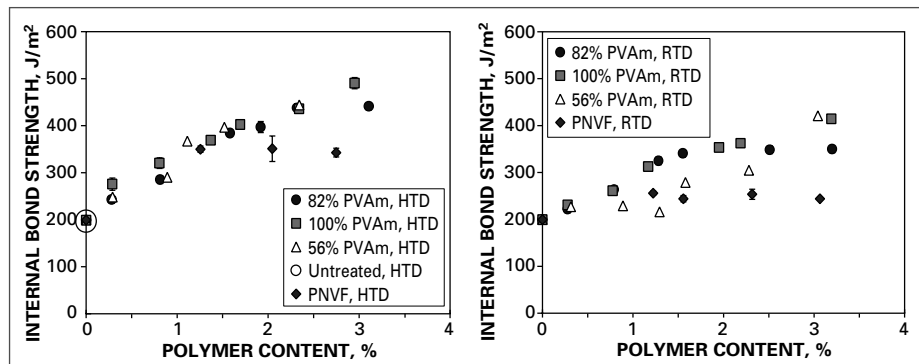
Trout's views on the importance of ionic bonds have been challenged. Espy states that quaternary ammonium polymers, such as polyDADMAC, can form ionic bonds but do not increase wet strength. Thus, he concludes that PEI achieves improvements in wet strength by forming covalent bonds through primary amine groups [23]. In his 1995 review of wet strengthening, Espy stated that the details of PEI wet strengthening mechanisms are unresolved [18]. These details remain unresolved for both PEI and PVAm wet-strength resins today.

CONCLUSIONS

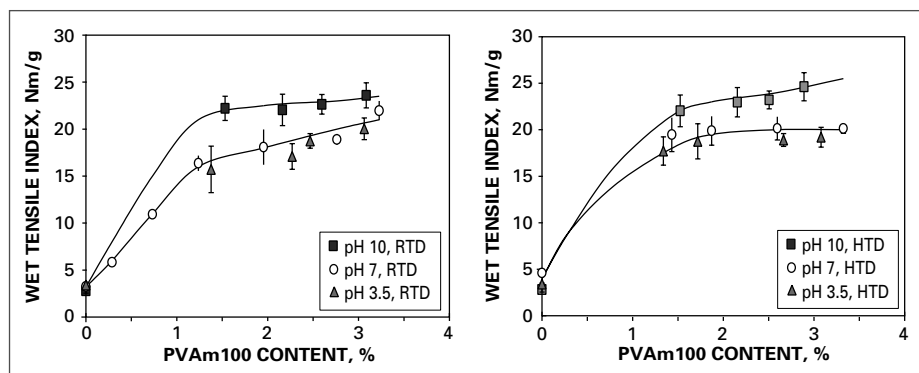
Poly(*N*-vinylformamide), polyvinylamine, and their copolymers increased the dry strength of newsprint. PNVF was slightly less effective as a dry strength agent than was PVAm and the copolymers.

PVAm increased the newsprint wet strength, whereas PNVF did not. The degree of hydrolysis was not very significant over the range of 56%–100%. Wet strength did not decrease with soaking time, which indicates that the increase is permanent.

We obtained similar improvements in strength by drying impregnated sheets both at room temperature and at 120°C. We recorded no strength improvements for never-dried, impregnated sheets. The wet and dry strengths of PVAm-impreg-



6. The influence of polymer addition on internal bond strength.



7. The influence of pH on wet strengthening.

nated sheets were highest at pH 10 and were slightly lower at pH 7 and pH 3.5.

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INSIGHTS FROM THE AUTHORS

We believe the day will come when all mechanical pulp sheets are surface treated. This work is a preliminary evaluation of a new candidate polymer for strengthening the surface of newsprint. The most difficult aspect of our research was preparing and characterizing the polymers. Although there are many papers that describe older polymer technologies, we think this report is the first published study in which polyvinylamine is evaluated as a wet strength resin for newsprint.

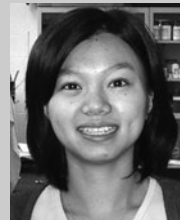
It is not obvious why polyvinylamine, a polymer that does react with cellulose, increases wet strength. None of the conventional mechanisms for improving wet strength explains this behavior.

Nevertheless, papermakers should consider polyvinylamine when developing grades based on surface-treated mechanical pulps. Our next step is to conduct fundamental investigations to try to understand the wet strengthening mechanism.

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