Polyvinylamine as a wet-end additive: Effects of pH and anionic contamination

MICHAEL S. LITAVECZ, SARAH PUTNEY, IAN J. SEIDEL, MORGAN E. DAVIS, FRANKLIN ZAMBRANO, AND MARTIN A. HUBBE

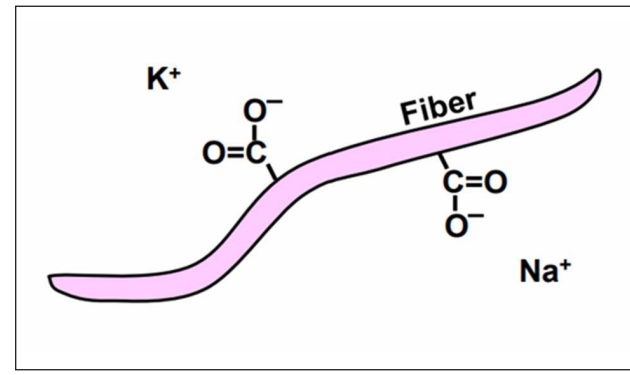
ABSTRACT: The effects of polyvinylamine (PVAm) on papermaking process attributes and handsheet quality were evaluated for a recycled copy paper furnish in a near neutral-to-alkaline pH range. The degree of protonation of primary amine groups, such as those in PVAm, is known to decrease with increasing pH. Streaming potential tests surprisingly showed that a high treatment level of PVAm on the copy paper furnish was able to maintain a net positive zeta potential up to pH of about 11, whereas charge demand titrations indicated that PVAm maintained its positive charge character up to about pH 10. Favorable dewatering was observed when the furnish had been pretreated with 1% polyacrylate dispersant prior to treatment with PVAm at the 0.5% level, and the mass of filtrate increased slightly with increasing pH. First-pass retention tests showed poor retention efficiency in systems where the furnish had been treated with the dispersant, then PVAm, in an unfavorable pH range of about 9 to 9.5. Higher retention was achieved both at pH 8.2 and at pH 10 or higher. Handsheets showed superior breaking length results in the systems where the stock had been pretreated with the dispersant, though strength decreased strongly with increasing pH. Differences in filler content, as indicated by ash analysis, were not large enough to account for the observed strength differences. Formation uniformity was substantially increased by the pretreatment with dispersant, even in the presence of PVAm and throughout the studied pH range.

Application: Due to its high cationic charge density and pH sensitivity, it is meaningful to test the performance characteristics of PVAm in a papermaking process. This work also sheds light on some unexpected interactions when PVAm was added to papermaking stock that had been intentionally contaminated with anionic dispersant.

Polyvinylamine (PVAm) is a water-soluble polymer having a positive charge, the magnitude of which depends on the pH of the solution [1]. Following the scale-up of methods for commercial synthesis of PVAm [2-3], it has been increasingly considered for various applications in papermaking [4-9]. For example, PVAm has been considered as a dry-strength additive [4-5], for achieving wet adhesion between cellulose surfaces [6], for antibacterial effects [7], and in studies related to fiber flocculation and the usage of nanofibrillated cellulose in papermaking [8-9]. In addition, papermaking applications have also been considered for a copolymer of PVAm having carboxylate groups [10].

Another reason to be interested in the performance of PVAm as a papermaking additive is its similarity to chitosan, which has received a lot of attention in papermaking research recently [11-14]. As in the case of PVAm, the nitrogen-based groups in chitosan are primary amine groups, the charge of which depends on pH.

One reason why there is interest in cationic polymer additives for papermaking systems is the net negative charge of typical fibers after pulping operations. As shown in **Fig. 1**, the negative charge of the fibers can be attributed to carboxylic acid groups [15-16]. In the case of bleached pulps, the major portion of these groups are associated with the hemicellulose component of the fibers. Due to attraction between charges having opposite signs, it is reasonable to expect effective retention of cationic additives on the fiber surfaces [17].



1. Representation of a cellulosic fiber, emphasizing the importance of carboxylic acid groups as an explanation for their predominantly negative charge within the usual pH range for papermaking.

It is known that the positive charge of amines (with the exception of quaternary amines) falls as the pH is increased in a range of about 4 to about 10, after which a neutral charge is shown [18]. Only limited research has been carried out to determine the effects of pH on the performance of papermaking additives based on primary amines, and some important questions remain. In particular, evidence has been presented suggesting that a bridging mechanism of interaction between surfaces in papermaking furnish

becomes dominant when these polyelectrolytes are used at neutral or higher pH values [11,19]. Most notably, the dry strength contribution of chitosan was found to be greater under alkaline conditions of papermaking (pH 8.5) [11]. In other words, conditions that would be expected to lead to a lower effective positive charge of the chitosan have led to more effective retention and strength effects. Some earlier studies had likewise shown that cationic polymers having a relatively low density of positively charged groups tended to be more effective for bridging flocculation [20] and for microparticle-type drainage and retention treatments [21] for papermaking.

The present research focused on alkaline papermaking conditions in which PVAm was used either alone or in combination with other additives. The key variable considered was the pH of the fiber suspension. Because of the presence of calcium carbonate filler in the recycled copy paper furnish that was used, most of the tests were constrained to pH values of about 8 and higher. As a further challenge to be addressed by the teams of undergraduate students carrying out the work, some of the furnish had been deliberately pretreated with an anionic dispersant (sodium polyacrylate) at a relatively high level. The purpose was to represent a high level of contamination, i.e., "anionic trash" or "dissolved and colloidal anionic materials." Such conditions can test the tolerance and robustness of various chemical additives systems for papermaking. Tested variables included zeta potential, charge demand, retention efficiency, drainage rates, degree of fiber flocculation, and resulting paper properties.

EXPERIMENTAL

Chemicals and materials

The chemical additives used in this work are listed in **Table I**, along with a general description and source information. The chemicals were diluted to 1% solids before use in the experiments. For purposes of calculations, the dry product was regarded as having 100% solids content. Further details regarding the chemicals, their preparation, and the experimental procedures were provided in a companion article [22].

Pulp preparation

Boise Aspen Recycled Multi-Use Paper (Packaging Corporation of America; Lake Forest, IL, USA), having 100% recovered fiber content, was used to make a 0.5% consistency pulp suspension. Based on 900°C ash analysis, the content of $CaCO_3$ in the paper was about 22.7% [22]. Sodium sulfate solution was added until the conductivity reached 1 mS/cm to simulate the typical salt buildup of some paper mill operations. Some of the default furnish, when noted in the results section, was pretreated at the 1% level (solid mass of additive on furnish solids) with the sodium polyacrylate dispersant.

Dewatering tests

A modified Schopper-Riegler test was used to measure the gravity-induced dewatering rates of pulp slurries under various conditions. A 200-mesh or 100-mesh screen was used to filter out fibers. The change to a coarser screen (100-mesh) was made in an effort to remove any influence of screen contamination on observed drainage rates. In future work of this type, the coarser screen is recommended for dewatering tests. The mass of fluid that had left the device was measured at 5 s, 10 s, 20 s, 40 s, and 60 s to observe how the dewatering rate changed over time.

Retention tests

Retention was measured using a Britt jar fitted with a 200-mesh screen. The slurry was mixed at 600 rpm. The slurry was sampled by removing the clamp at the bottom orifice. The first 10–20 mL of filtrate collected was dumped back into the Britt jar. A second sample was collected and diluted by a factor of 10. The turbidity of the diluted second sample was measured ten times. The system was assumed, as a first approximation, to follow the Beer-Lambert law, such that turbidity is proportional to the solids present in the suspension [23-24]. The turbidity of the slurry was calculated as ten times the average turbidity of the diluted filtrate samples.

Flocculation tests

In this test, 500 mL of stirred stock solution was pumped through a 6-mm inner diameter Tygon® tube (Saint-Gobain; Courbevoie, France) at a rate of 50 mL/min. A "low-gain" photometric dispersion analyzer (PDA) from Rank Brothers (Newbury, England) measured the amount of flocculation in the slurry. The root-mean-square (RMS) values were recorded with the "Filter" mode selected, with the gain constants both set at 1.000.

Brand Name	Supplier	Description
Hercobond 6350	Solenis[1]	Polyvinylamine (PVAm) dry strength technology
Sokalan PA 40	BASF[2]	Sodium polyacrylate, dispersant

1. Solenis LLC (Wilmington, DE, USA)
2. BASF (Ludwigshafen, Germany)

I. Chemicals used in the experiments.

Streaming potential tests

In this test, a vacuum was applied through a 100-mesh screen to separate filtrate from stirred stock. A millivoltmeter measured the change in voltage (potential) across the fiber pad. The zeta potential (ζ) was found by comparing the voltage versus the change in applied pressure and using the Helmholtz-Smoluchowski equation [25-26], as follows:

$$\zeta = 4\pi \Delta E \eta\lambda / (\Delta P \varepsilon)$$

where ΔE is the measured difference in voltage between the probes, η is the viscosity, λ is the electrical conductivity, ΔP is the applied vacuum, and ε is the dielectric constant. For convenience, the following form of the equation, with temperature corrections for viscosity of water and electrical conductivity (relative to 25°C calibration), was used:

$$\zeta \text{ (mV)} = 12.27\ \Delta E \text{ (mV)} * [\lambda \text{ (µS/cm)} / \Delta P \text{ (mm Hg)}] * [1+(25-\theta)/44.74)]/ [1+(25-\theta)/223.7)]$$

Charge demand titrations

An emtec CAS touch! streaming current detector (emtec Electronic; Leipzig, Germany) was used to measure the charge demand, and 0.001 N solutions of poly(diallyldimethylammonium chloride) and poly(vinyl sulfate) were used as titrants.

Handsheet formation and testing

Handsheets were made and tested using TAPPI Standard Test Methods T 205 "Forming handsheets for physical tests of pulp" and TAPPI T 220 "Physical testing of pulp handsheets," respectively.

Tensile testing

Tensile testing was conducted following TAPPI Methods T 494 "Tensile properties of paper and paperboard (using constant rate of elongation apparatus)" and TAPPI T 220. A 15-mm-wide strip of paper was cut from the center of the handsheet. It was set in the jaws of the tensile tester, which were 100 mm apart. The device pulled the strip apart, and the strength data from the machine were collected.

Air permeability

A manual Gurley densometer was used to measure the air permeability of the handsheets following TAPPI T 460 "Air resistance of paper (Gurley method)." The inner cylinder was raised until it was supported by the latch at the top of the device. A handsheet was inserted into the device and secured. Then, the catch holding the inner cylinder was released, and the time for 100 cm^3 of air to flow through the handsheet was recorded.

Formation uniformity

The Paper PerFect Formation Analyzer (OpTest Equipment; Hawkesbury, ON, Canada) was used to measure the average floc size of the handsheets. Testing focused on two floc size ranges, C7 (6.7–13 mm) and C9 (18.5–31 nmm).

Ash content

The ash content of the handsheets was tested. As described in TAPPI T 413 "Ash in wood, pulp, paper and paperboard: combustion at 900°C," the handsheets were weighed and put in a 900°C oven for 1 h, then removed and weighed again after cooling. The handsheets were assumed to have a 10% moisture content going into the oven (air dry). The percentage of ash content was calculated as follows:

Ash (%) = [Ash weight (g) / (0.9 * Oven-dry paper weight (g))] * 100%

RESULTS

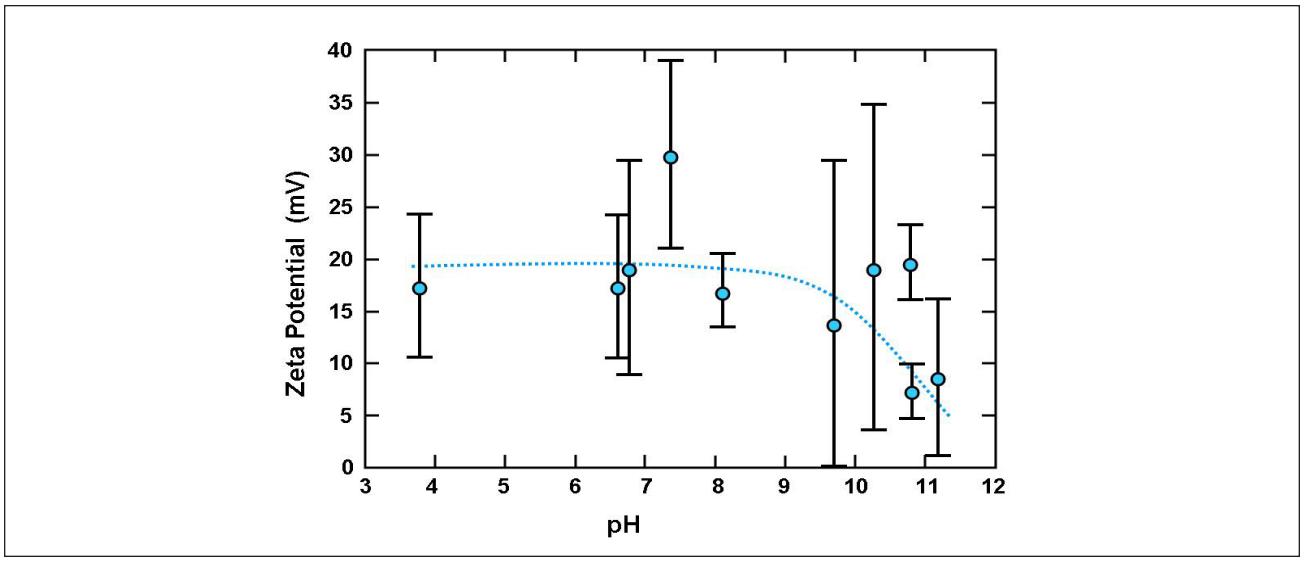
Zeta potentials

The effects of pH on the zeta potential of a furnish treated with 1% on solids PVAm are shown in **Fig. 2**. The relatively large scatter in measured results is attributed to the realistic amount of salinity (1 mS/cm) of the furnish, which repressed the signal. The dotted line indicates the main trend. The zeta potential of the furnish was positive throughout the entire range tested, from an acidic to basic pH range. Especially at the lower end of the pH range, such findings are consistent with the cationic nature and high charge density of PVAm. However, in the light of previous findings [18], it was surprising that the zeta potential remained positive in the higher pH range, especially above a pH of 10. A possible explanation may lie in the high density of amine groups within PVAm. Thus, even if only a small fraction of them remain protonated at a certain high pH value, it might still be enough to outnumber the negatively charged carboxylate groups present on the fibers.

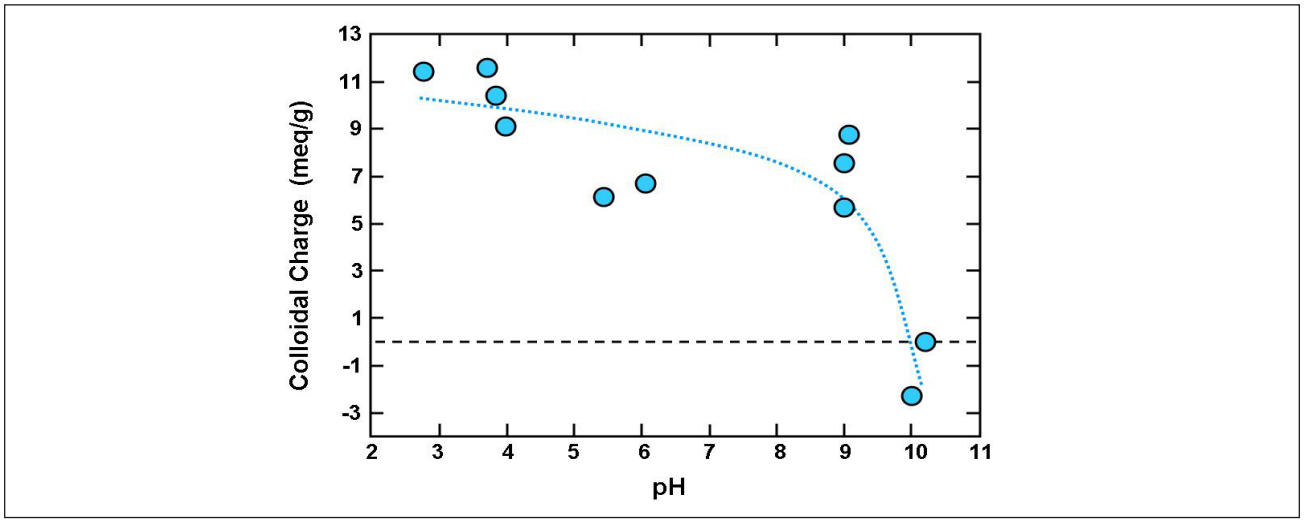
Charge demand properties

The results of the cationic demand testing of PVAm alone in water are shown in **Fig. 3**. The cationic charge of the polymer solution generally decreased with increasing pH. The values dropped rapidly to zero as the pH reached about 10. The results are consistent with what is expected for the deprotonation of primary amine groups with increasing pH [17].

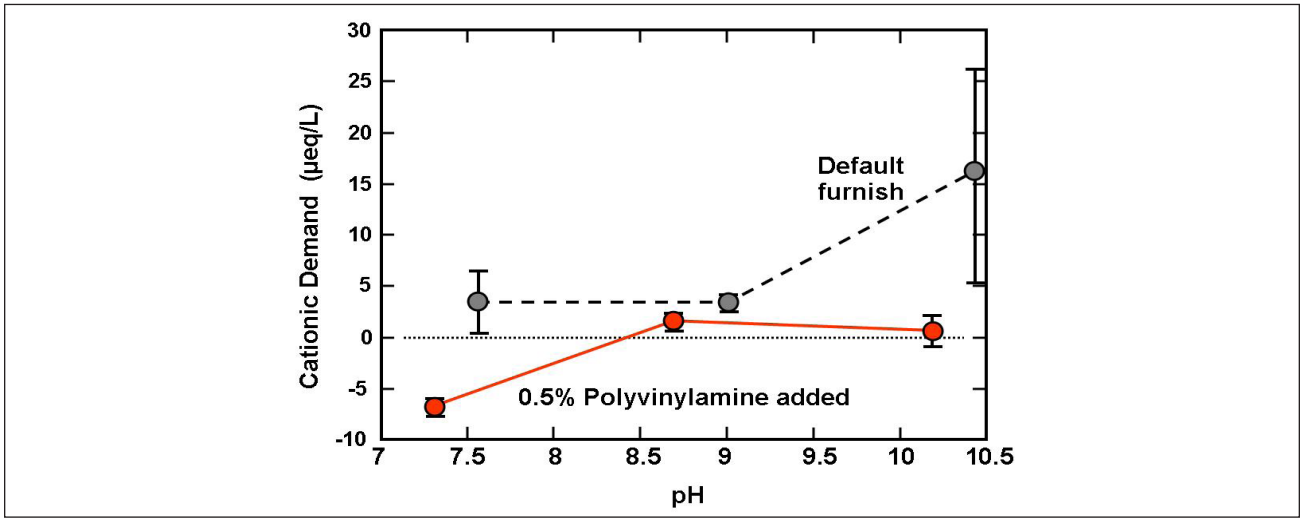
Figure 4 shows corresponding cationic demand results for the default furnish. In an untreated pulp furnish at neutral to basic conditions, the cationic demand of the filtrate was net positive due to the negative carboxyl groups on the surfaces of fibers, as well as colloidal material from the fibers. With the addition of highly cationic PVAm, the cationic demand was made either less positive or more negative. The PVAm was able to neutralize the cationic demand of the furnish at a higher pH of around 10.2, although there was a large error in the default furnish results at the highest tested pH value.



2. Effects of pH on zeta potential of a 1% on solids polyvinylamine (PVAm) treated furnish.



3. Effects of pH on the colloidal charge of PVAm in aqueous solution.



4. Effects of pH on cationic demand on an untreated furnish and a furnish with the addition of 0.5% on solids PVAm.

A surprising aspect of the results for the 0.5% PVAm condition in Fig. 4 was that positive values for cationic demand (meaning a net-negative charge of the filtrate) were observed under conditions where the corresponding zeta potential results in Fig. 3 showed net positive fiber surfaces. Here, it is important to note that the two tests measure different things. The streaming potential tests (Fig. 3) show information about the fiber surface. The charge demand titration results (Fig. 4) show information about dissolved and colloidal material in the filtrate. In theory, one would expect that processes of mixing and adsorption would cause the fiber surfaces to become negative whenever the cationic demand is positive. Further work may be needed in order to explain these findings.

Dewatering rate testing

The two curves shown in **Fig. 5**, having to do with dewatering, need to be considered separately, since the corresponding tests were carried out with different screens. A finer 200-mesh screen was used just for the tests with the default furnish, but it was replaced by a coarser 100-mesh screen for the remaining tests.

The lower curve corresponds to treatment of the default furnish with 0.5% PVAm. There were two peaks corresponding to higher drainage. Such higher dewatering rates were observed at the default pH (8.2) and also in furnish pH adjusted to a high pH of 10.5 before the PVAm addition. Slower drainage was observed in the intermediate pH range.

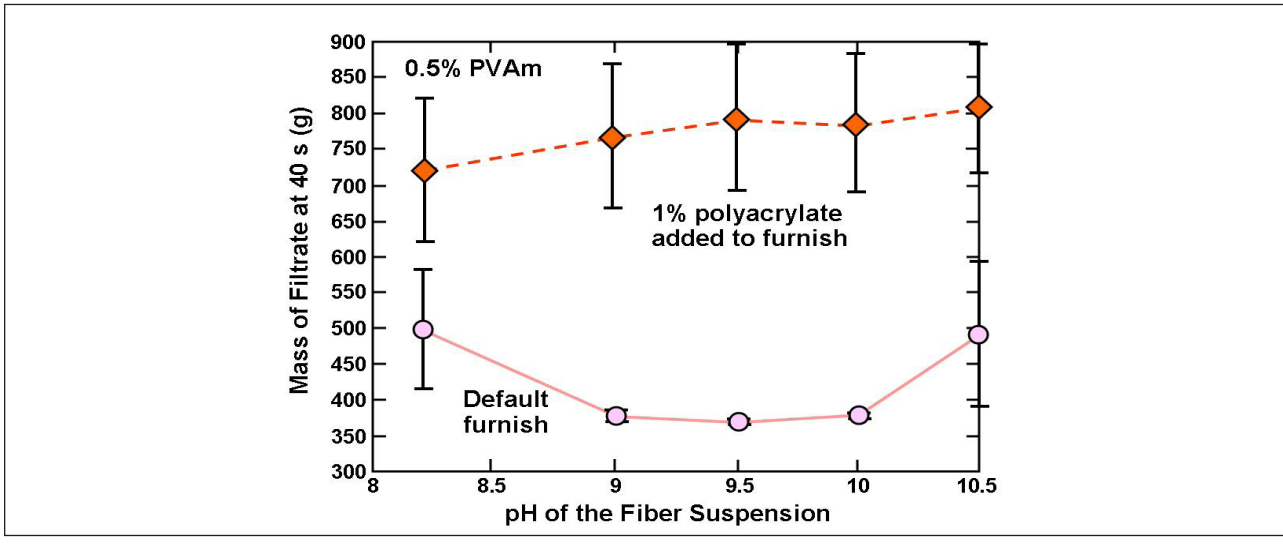
The upper curve reveals something that has not been reported in previous work. Relative to the data reported by Putney et al. [22], it shows that pretreatment of the furnish with polyacrylate dispersant at a relatively high level (1%) yielded favorable dewatering upon addition of the 0.5% PVAm. The effect was persistent over a wide pH range (all "alkaline papermaking" conditions).

Retention efficiency

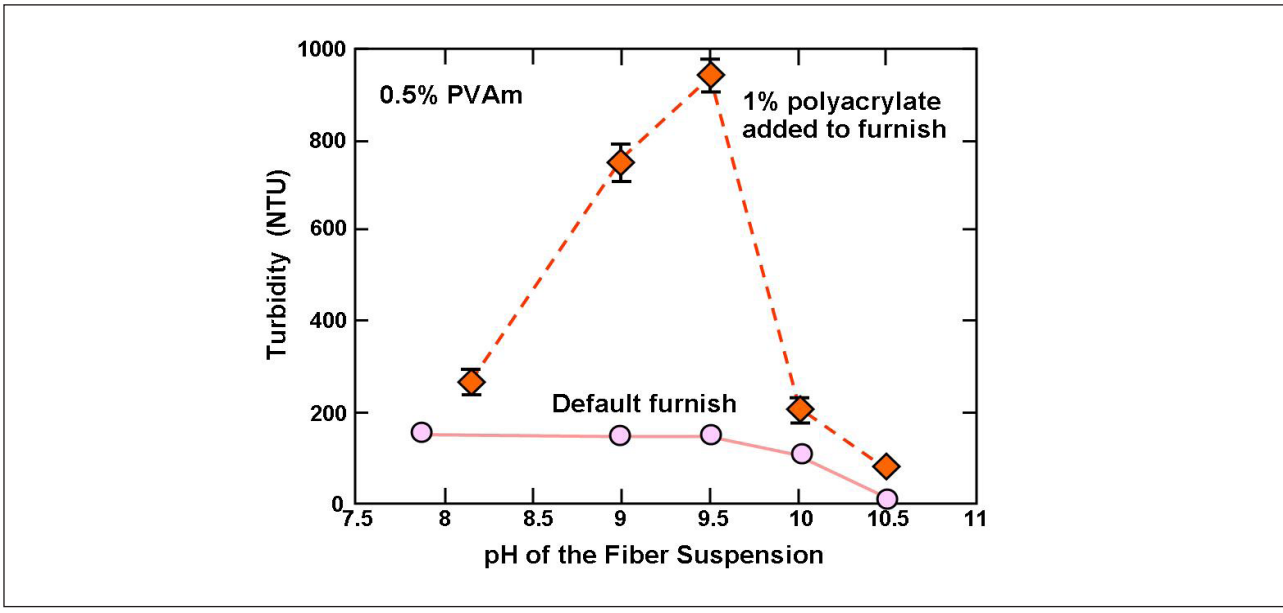
Results of the retention tests are shown in **Fig. 6**. Lower turbidity values of the filtrate indicate higher retention of fine particles. Error bars are shown only in cases where the 95% confidence limits were larger than the corresponding plotted point. It was found that while changes in pH under ordinary alkaline papermaking conditions did not affect the retention performance of PVAm, it was very effective at the highest pH level tested. Past researchers have argued that such results (often observed with chitosan) are due to the polymer exhibiting a bridging mechanism [11,19].

Unexpected results were shown by the upper curve, where polyacrylate dispersant had been added to the furnish. The deeper red of the diamond symbols reminds us that the polyacrylate dispersant makes the system more anionic. High retention was obtained near pH = 8.2, which is typical for alkaline papermaking conditions. This might be attributed to polyelectrolyte complexation between the polyacrylate (1%) and the PVAm (0.5%). High retention achieved at the highest pH values would support the statements made earlier regarding a possible bridging mechanism.

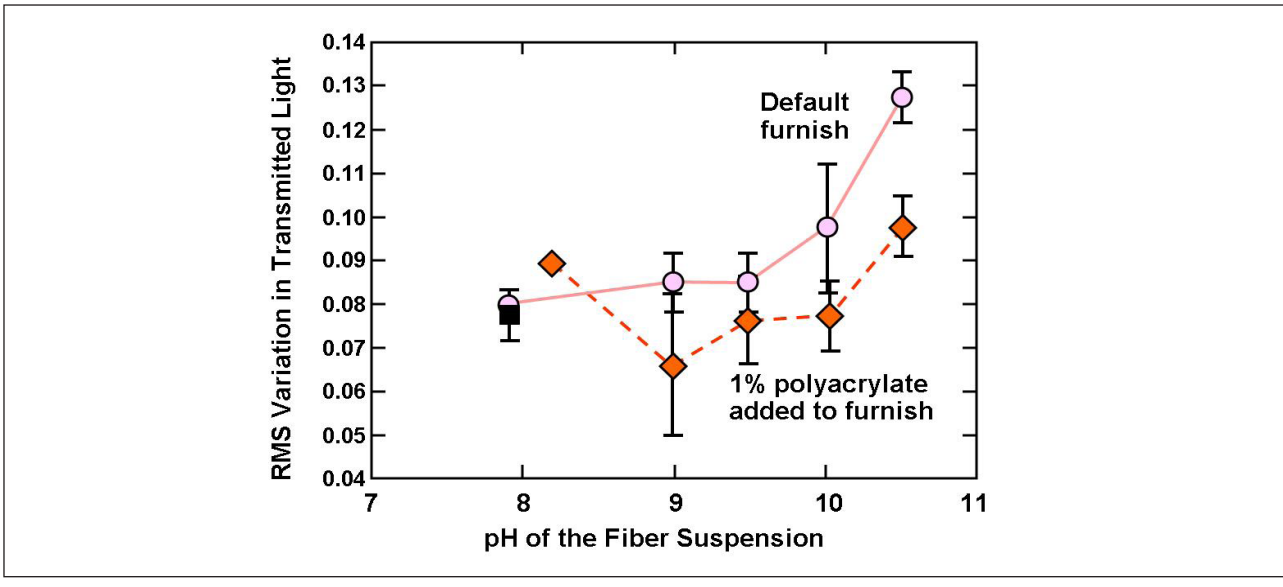
In an attempt to understand the results just described, a pair of working hypotheses will be proposed and tested. First, it would be expected that in the presence of dispersant, the PVAm would be become less effective as a retention agent with increasing pH due to the decreasing positive colloidal charge of the amine groups. This concept is supported by the increasing turbidity of the filtrate as the pH was increased from 8.2 to 9.5. To account for the subsequent improvement in retention, with further increase in pH, it is initially proposed that this is due to increased ionic strength. It is well known that an increased ionic strength will suppress the range and strength of electrostatic repulsive forces between like-charged objects in a suspension [27]. On



5. Mass of filtrate drained after 40 s at varying pH levels for 0.5% PVAm treated furnish. Red diamond symbols correspond to furnish pretreated with 1% dispersant. Pink circles correspond to the default furnish.



6. Turbidity measurement of a PVAm treated furnish with and without the addition of 1% polyacrylate.



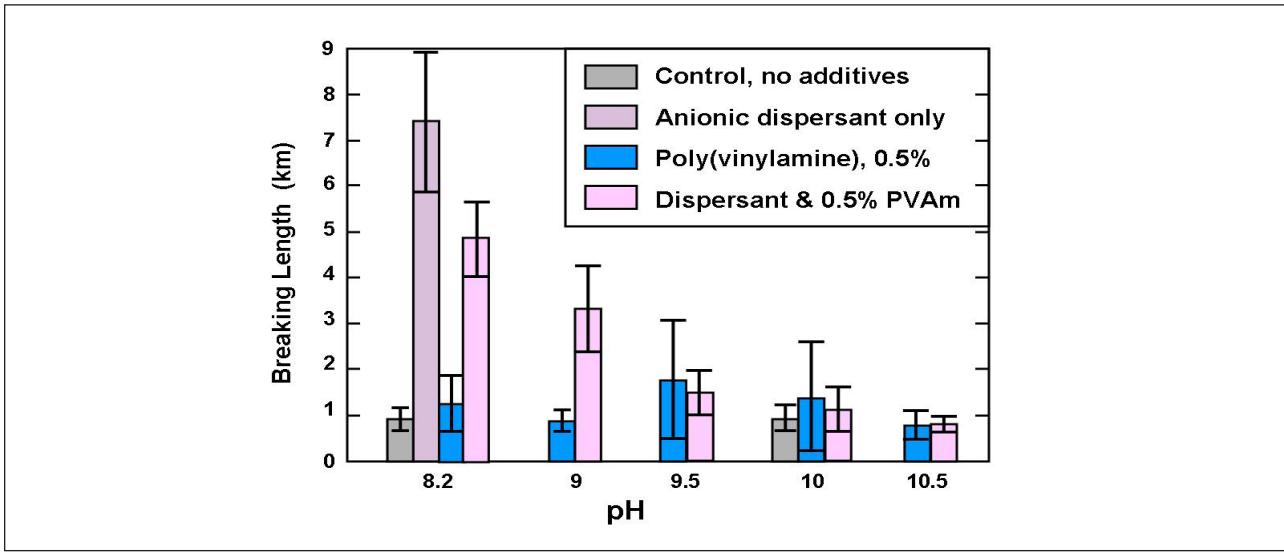
7. Flocculation measurement of a PVAm treated furnish with and without the addition of 1% on solids polyacrylate dispersant. The black square corresponds to the untreated blank (RMS: root mean square).

that basis, adding sufficient sodium hydroxide (NaOH), and thereby increasing the ionic strength, would be expected to increase the retention of fine particles onto fiber surfaces. In the present case, however, this second hypothesis can be rejected. The reason is that the process water already had been treated with sodium sulfate at a sufficiently high level that a pH of 10 or 10.5 would have only a minor relative effect on the ionic strength.

Fiber flocculation

Figure 7 compares the flocculation of two stock suspensions following treatment with 0.5% PVAm. One of the suspensions had been pretreated with the dispersant, while the other had not. The tests were conducted over a pH range from near-neutral to highly alkaline. Results showed a high level of flocculation of the PVAm systems at the highest reported pH. Though this observation has not been reported before, it seems consistent with earlier theories of bridging flocculation by amine-type polymers at high pH values [11,19].

The findings for flocculation in systems where PVAm was added last can be regarded as generally favorable. The pretreatment with polyacrylate dispersant, which seemed favorable for both drainage and retention (when PVAm was used), did not produce excessive flocculation, especially at typical pH for alkaline papermaking, e.g., pH = 8.2.



8. Results of breaking length testing on handsheets.

Handsheet properties

Figure 8 shows the results of breaking length tests. As indicated, the addition of polyacrylate dispersant to the default furnish greatly increased the breaking length. This effect can be best shown at a pH of 8.2, where the addition of the dispersant alone increased the breaking length to over 7 km (from the control value of 1 km). The addition of PVAm alone did not appear to significantly affect the breaking length of the handsheets. The combination of the dispersant and PVAm increased the breaking length beyond that of the control at the lower ranges of pH's tested (8.2–9), but not to the same extent as using the dispersant alone. Increasing the pH decreased the breaking length of handsheets dosed with PVAm and anionic dispersant.

Results for air permeability and ash tests are shown in **Table II**. The addition of 0.5% PVAm significantly increased the ash content of the handsheets across the entire neutral-to-basic pH range tested, with slight increases in air permeability (although not significantly different from

pH	Dispersant, %	PVAm, %	Gurley Densometer, s/100 cm³		900°C Ash, %	
			Mean	St. Dev.	Mean	St. Dev.
8.2	0	0	12.7	1.31	3.5	0.26
8.2	0	0.5	11.2	3.08	9.5	0.33
9	0	0.5	9.9	0.59	9.1	0.34
9.5	0	0.5	10.8	0.91	8.9	0.24
10	0	0.5	8.8	0.99	10.4	1.97
10.5	0	0.5	10.3	1.19	9.3	0.41
8.2	1	0	6.2	5.53	3.3	0.09
10	1	0	4.6	1.34	-	-
8.2	1	0.5	1.6	0.28	5.9	0.35
9	1	0.5	5.6	0.63	6.2	0.24
9.5	1	0.5	5.2	1.33	5.6	0.35
10	1	0.5	4.0	2.05	6.2	0.65
10.5	1	0.5	3.0	1.98	6.2	0.48

II. Air permeability and percent ash content of handsheets (PVAm: polyvinylamine).

pH	Dispersant, %	PVAm, %	C7 Mean	Standard Deviation	C9 Mean	Standard Deviation
8.2	0	0	18.3	2.07	29.1	4.14
10	0	0	12.3	0.05	21.2	0.90
8.2	0	0.5	14.5	0.99	25.5	1.78
9	0	0.5	12.0	0.57	21.1	1.29
9.5	0	0.5	11.0	0.15	18.4	0.32
10	0	0.5	10.8	0.15	18.4	0.15
10.5	0	0.5	10.5	0.59	17.8	0.92
8.2	1	0	20.6	1.19	40.5	2.10
8.2	1	0.5	20.1	0.26	39.4	0.64
9	1	0.5	19.7	0.15	38.7	0.55
9.5	1	0.5	19.5	0.13	39.7	0.34
10	1	0.5	19.4	0.06	39.5	0.39
10.5	1	0.5	19.5	0.24	39.5	0.19

III. Results of formation uniformity testing Paper PerFect formation analyzer.

the control). The addition of the 1% dispersant significantly increased the air permeability of the handsheets, with a small decrease in ash content. The combination of the dispersant and PVAm greatly increased the air permeability of the handsheets (lower Gurley seconds). This effect was greatest at a pH of 8.2, where the permeability was over ten times greater than that of the control. At higher pH values, the effects of the additives were less pronounced, with air permeability being only two to three times greater than that of the control handsheets. The relatively high air permeability of sheets from stock that had been pretreated with anionic dispersant is in agreement with the relatively high dewatering rates shown earlier in Fig. 4 for those same conditions.

The results of formation uniformity testing are shown in **Table III**, with higher values indicating more uniform formation. Increasing the pH decreased the uniformity of the control and PVAm-treated handsheets, with this effect being less pronounced on handsheets that had been pretreated with the polyacrylate dispersant. In general, the addition of PVAm decreased the uniformity of the handsheets. Addition of the polyacrylate dispersant at the 1% level on solids in the absence of other additives greatly increased the uniformity of the handsheets. When the dispersant was used in combination with PVAm, it was able to counteract the decrease in formation uniformity caused by PVAm. Thus, a high uniformity was maintained across the entire neutral-to-basic pH range tested when the system had been pretreated with the dispersant.

DISCUSSION

Though laboratory testing of papermaking systems is inherently simpler than what happens on a commercial paper machine, this study included some features aimed towards making conditions more realistic. The furnish, which was prepared from 100% recycled copy paper, can be expected to contain a range of fibers, cellulosic fines, filler particles, and a baseline of chemical additives that had been employed during the initial production cycle. In addition, the tests were carried out in the presence of water that had been adjusted to a realistic electrical conductivity level of 1000 µS/cm by the addition of sodium sulfate. In an attempt to observe some effects related to contamination with anionic colloidal material (sometimes called anionic trash), some batches of the default furnish were pretreated at the 1% level (by solids) with an anionic dispersant. On the other hand, with an aim to clearly reveal effects of chemical treatments, the dosage levels used in the present work were often large in comparison to common commercial practices.

When evaluating effects in the default furnish, the dewatering rate effects showed some agreement with earlier work that had indicated different mechanisms acting at different ranges of pH [11,19]. Accordingly, a significantly higher dewatering rate at the highest pH considered (about 10.5) of the untreated stock seems consistent with a bridging mechanism of flocculation by the PVAm, due to its low cationic charge at that pH. By contrast, a charge neutralization mechanism is reasonable as a way to explain increases in drainage rates at the lowest pH level considered

(about 8.2), corresponding to the self-buffered pH of the default furnish. Notably, the highest pH values also led to higher levels of flocculation and retention efficiency in the present work.

As already mentioned in a companion article [28], the observed effects due to the addition of the polyacrylate dispersant at the 1% level based on solids appear to fall outside of the range of conventional papermaking, and the authors are not aware of other studies showing apparent high dewatering rates following such treatment. Though the results shown in Fig. 5 suggest a positive effect on drainage, these results are not consistent with those reported earlier, when evaluating a range of tissue additives in the same type of furnish [22]. The mesh screen used on the modified Schopper-Reigler device was periodically removed for scrubbing with soap and water, and/or replaced, due to gradual accumulation of fine material in the course of multiple experiments. In particular, tests involving pretreatment with the dispersant were always done on different days and by different experimenters from those who studied the furnish in the absence of dispersant.

A question that might be considered in future work is whether or not a combination of treatment with a cationic polymer, followed by an anionic dispersant, at optimized levels, might achieve drainage benefits analogous to combinations of cationic polymers such as retention aids, followed by colloidal silica or bentonite [29]. The present experiments were not sufficient to shed light on that possibility. Earlier work, which led to commercial products, showed that such effects can be achieved with certain highly crosslinked anionic polyelectrolytes being used in place of the negatively charged nanoparticles or microparticles [21]. However, questions remain regarding the ranges of material that can be employed to achieve drainage benefits by related sequential combinations of oppositely charged additives.

When considering the retention results, certain aspects of the pH-related results were once again in apparent agreement with earlier findings [11,19]. Thus, it might be proposed that, in the systems pretreated by dispersant, it would be reasonable to expect poor results in a pH range that was too high for the PVAm to be effective as a charge neutralizing agent, but too low for it to have its best effect as a bridging flocculant. Such a mechanism is also consistent with the nature of the polyacrylate dispersant. Its charge density would be expected to become increasingly anionic with increasing pH over a range from about 3 to neutral pH, and then to remain steady over the range considered in this study.

Availability of equipment allowed for some key observations regarding formation uniformity that had not been considered in two companion articles [22,28]. The results showed relatively large numerical improvements in formation uniformity upon pretreatment of the furnish with the anionic dispersant, and much lesser decreases in formation uniformity with subsequent PVam addition, regardless of pH level. For many papermakers, utilization of dispersants would be regarded as undesirable, not only due to the added expense, but also due to strong interferences with the action of retention aids. Nevertheless, the present results suggest that PVAm might be a suitable choice of agent for dispersant-treated furnish as a way to achieve acceptable retention results, good drainage, good formation uniformity, and favorable strength.

CONCLUSIONS

Effects of polyvinylamine, alone and in combination with other papermaking additives, were evaluated when it was added to furnish prepared from recycled copy paper. To simulate a highly contaminated system, some of the furnish had been pretreated at a high level with anionic dispersant. Operational outcomes such as drainage rates, retention efficiency, and flocculation tendency were tested, in addition to tensile, strength, porosity, formation uniformity, and ash content of the resulting paper.

Many of the effects of PVAm addition could be explained based on its cationic charge, in addition to the pH-dependency of that charge. The zeta potential of the fibers treated by PVAm at a suitable level remained positive up to a pH of 11, which is higher than was expected based on the literature. Charge demand titrations showed decreasing cationic charge with increasing pH, reaching a zero value at about pH 10.

Adding sodium polyacrylate dispersant at a 1.0% level to the furnish (based on solids) led to high strength characteristics of the paper, in addition to favorable drainage. These results appeared to be associated with very uniform formation, as well as lower filler content of the resulting sheets. Addition of PVAm at the 0.5% level in such systems was able to improve the retention of filler, while still achieving relatively high strength, as well as good dewatering and favorable uniformity.

In the typical pH range for alkaline papermaking, in the absence of dispersant, the effects of PVAm addition were generally consistent with charge-related mechanisms, such as charge neutralization or polyelectrolyte complexation. The retention performance of PVAm was independent of pH within a pH range from about neutral to about 9.5. At yet higher pH values, its effects on retention and drainage increased. These results, though they seem to be in agreement with some earlier reported findings, have not yet been fully explained. Notably, however, the unexplained behaviors were seen only for pH conditions outside of the pH range commonly used in paper mills.

ACKNOWLEDGEMENTS

The experimental work reported in this article represents the efforts of members of the Fall 2022 class of PSE 322, "Wet End & Polymer Chemistry," at North Carolina State University. These students, who included Corey Helseth,

Bailey Reed, Michael Tozer, Lucy Huitt, Cami Clickner, Carmeron Pate, Rick Conner, Rylee Sepesi, Kaleb Estridge, Tate Lee, Sydney Ford, Genevieve Gauthier, Trae Knight, Eetu Jooseppi Toikka, Aidan Stewart, Maggie Lawler, Samuel Wolfe, Bryanna Lawry, Bennett Surrett, Sami Anthony, and Sydney Crush, are acknowledged for these contributions to the present work. The student co-authors Sarah Putney, Ian Seidel, Michael Litavecz, and Morgan Davis contributed to the work during the semester and also completed follow-up experiments, discussed the interpretation of the findings, and contributed to the writing. The work of Dr. Hubbe is supported by the Buckman Foundation

LITERATURE CITED

1. Linhart, F. and Auhorn, W., *Papier* 46(10A): V38(1992).
2. Lorencak, P., Stange, A., Niessner, M., et al., *Wochenbl. Papierfabr.* 128(1-2): 14(2000).
3. Pinschmidt, R.K., *J. Polym. Sci., Part A: Polym. Chem.* 48(11): 2257(2010). https://doi.org/10.1002/pola.23992.
4. Wang, J.A., Yu, L.F., and Lian, A.F., "Application of polyvinylamine as paper strengthening agent," in *Research Progress in Paper Industry and Biorefinery (4th ISETPP)* (R.C. Sun and S.Y. Fu, Eds.), China Scientific Books, Wan Chai, Hong Kong, 2010, pp. 1594.
5. Sjöstrand, B. and Brolinson, A., *BioResources* 17(3): 4098(2022). https://doi.org/10.15376/biores.17.3.4098-4115.
6. Yang, D., Stimpson, T.C., Soucy, J., et al., *Cellulose* 26(1): 341(2019). https://doi.org/10.1007/s10570-018-2165-9.
7. Lee, J., Kim, S.S., Sim, K., et al., *BioResources* 13(1): 241(2018). https://doi.org/10.15376/biores.13.1.241-255.
8. Merayo, N., Balea, A., de la Fuente, E., et al., *Cellulose* 24(2): 677(2017). https://doi.org/10.1007/s10570-016-1138-0.
9. Merayo, N., Balea, A., de la Fuente, E., et al., *Cellulose* 24(7): 2987(2017). https://doi.org/10.1007/s10570-017-1302-1.
10. Wang, S.L., Wang, M., and Chen, F.S., *BioResources* 10(1): 750(2015). https://doi.org/10.15376/biores.10.1.1869-1878.
11. Rohi, M., Ramezani, O., Rahmaninia, M., et al., *Cellul. Chem. Technol.* 50(7-8): 873(2016).

ABOUT THIS PAPER

Cite this article as:
Litavecz, M.S., Putney, S., Seidel, I.J., et al., *TAPPI J.* 23(5): 237(2024). https://doi.org/10.32964/TJ23.5.237

DOI: https://doi.org/10.32964/TJ23.5.237

ISSN: 0734-1415

Publisher: TAPPI Press

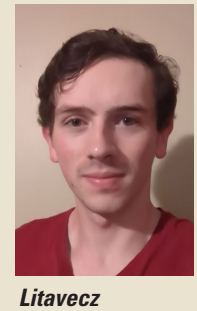
About this journal

ABOUT THE AUTHORS

We studied this topic because we had seen some reports in the literature about unusual effects of pH on the effectiveness of polyvinylamine (PVAm) relative to its charge and its papermaking effects. However, this information seemed incomplete. The new information that we have provided gives a much fuller and more nuanced picture. It confirms many of the earlier findings, but gives more context.

We found it challenging to account for what happens during industrial production by use of laboratory studies, so attention to detail was necessary for addressing this. We found that with the help of a team of undergraduate researchers, it is possible to accumulate sufficiently full experimental evidence to follow up on such important questions as this that need answers.

Polyvinylmaine has become quite widely used in the paper industry. Thus, the information that we are providing will be helpful to both chemical suppliers and to specific paper mill teams. In the future, the team and North Carolina State University will continue to research additional under-studied areas of papermaking chemical technology.



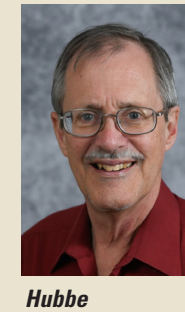
Litavecz

Putney

Seidel

Davis

Zambrano



Hubbe

Litavecz, Putney, Seidel, and Davis are undergraduate students in the Paper Science and Engineering program and Hubbe is professor in the Department of Forest Biomaterials at North Carolina State University, Raleigh, NC, USA. Zambrano, a Ph.D. graduate of the same program, is affiliated with Solenis LLC and is located at their research facility in Wilmington, DE, USA. Email Hubbe at hubbe@ncsu.edu.

12. Rahmaninia, M., Rohi, M., Hubbe, M.A., et al., *Carbohydr. Polym.* 179: 328(2018). https://doi.org/10.1016/j.carbpol.2017.09.036.
13. Amiri, E., Rahmaninia, M., and Khosravani, A., *BioResources* 14(4): 7687(2019). https://doi.org/10.15376/biores.14.4.7687-7701.
14. Rohi Gal, M., Rahmaninia, M., and Hubbe, M.A., *Carbohydr. Polym.* 309: 120665(2023). https://doi.org/10.1016/j.carbpol.2023.120665.
15. Laine, J. and Stenius, P., *Pap. Puu* 79(4): 257(1997).
16. Hubbe, M.A., Sundberg, A., Mocchiutti, P., et al., *BioResources* 7(4): 6109(2012). https://doi.org/10.15376/biores.7.4.6109-6193.
17. Poptoshev, E., Rutland, M.W., and Claesson, P.M., *Langmuir* 16(4): 1987(2000). https://doi.org/10.1021/la990961v.
18. Halverson, F., "Retention aids, drainage aids, and flocculants," in *Chemical Processing Aids in Papermaking: A Practical Guide*, TAPPI Press, Atlanta, 1992, Ch. 8, pp. 103-127.
19. Li, H.B., Du, Y.M., and Xu, Y.M., *J. Appl. Polym. Sci.* 91(4): 2642(2004). https://doi.org/10.1002/app.13444.
20. Hubbe, M.A., *Colloids Surf.* 25(2-4): 325(1987). https://doi.org/10.1016/0166-6622(87)80312-8.
21. Moffett, R.H., *Tappi J.* 77(12): 133(1994).
22. Putney, S., Seidel, I.J., Litavecz, M.S., et al., *TAPPI J.* 23(2): 67(2024). https://doi.org/10.32964/TJ23.2.67.
23. Milliken, J.O., "Spectrophotometric determination of fines retention using the Dynamic Retention/Drainage Jar," *TAPPI Seattle Retention and Drainage Short Course*, TAPPI Press, Atlanta, 1977, pp. 55-57.
24. Ricci, R.W., Ditzler, M.A., and Nestor, L.P., *J. Chem. Educ.* 71(11): 983(2004). https://doi.org/10.1021/ed071p983.
25. Helmholtz, H., *Ann. Phys. Chem.* 7: 337(1879). https://doi.org/10.1002/andp.18792430702.
26. Smoluchowski, M. von, *Bull. Int. Acad. Sci. Cracovie* 3: 184(1903).
27. Hubbe, M.A. and Rojas, O.J., *BioResources* 3(4): 1419(2008). https://doi.org/10.15376/biores.3.4.1419-1491.
28. Seidel, I.J., Litavecz, M.S., Putney, S., et al., *TAPPI J.* 23(2): 78(2024). https://doi.org/10.32964/TJ23.2.78.
29. Hubbe, M.A., "Microparticle programs for drainage and retention," in *Micro and Nanoparticles in Papermaking* (J.M. Rodriguez, Ed.), TAPPI Press, Atlanta, 2005, Chap. 1, pp. 1-36.