APPLICATION OF POLYALLYLAMINE AS A DRY STRENGTH AGENT FOR PAPER

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ABSTRACT

Dry strength is an inherent structural property of a paper sheet. It is due primarily to the development of fiber-to-fiber bonds. Polyamines, especially polyallylamine, were found to be suitable mordants for rosin sizing. However, their effectiveness as dry strength agents has not been studied. In this study polyallylamine·HCl (PAA) was found to be an effective dry strength agent. With unbleached kraft pulp, 0.5% PAA on mass of oven dry pulp was sufficient to increase the dry strength of handsheets, while bleached kraft pulp required more PAA based on the mass of oven dry pulp. Different strength properties were measured and it was found that the largest increase was in the folding endurance of the handsheets. The strength properties were highly dependent on the drying conditions of the handsheets.

In this paper dry strength development is discussed based on the interaction between protonated (cationic) PAA and the cellulosic fibers and between the interaction of the cationic amine and the aromatic π-bonding of lignin. PAA was effective as a dry strength agent and the bursting strength, folding endurance and the tensile strength increased for handsheets made from different types of pulps using polyallylamine·HCl. PAA is a promising material that may offer superior performance in some specialized applications.

INTRODUCTION

Paper is essentially a laminated structure composed of cellulose fibers and bonds between these fibers. Dry strength is an inherent structural property of a paper sheet, which is due primarily to the development of fiber-to-fiber bonds during consolidation and drying of the fiber network. Paper strength is dependent on the strength of individual fibers, the strength of interfiber bonds, the number of bonds (bonded area) and the distribution of fibers and bonds (formation) (1). Fiber-to-fiber bonds are usually weaker than the strength of individual fibers until the latter become the limiting factor in a well-bonded sheet (2). Paper strength additives may bring about improvement in one or more of the above factors, although it may be assumed that they are unlikely to affect the strength of single fibers.

*The research was conducted at Oregon State University

Mechanical entanglement leading to fiber flocculation is the first step in a long chain of events forming the stable network of fiber. Various forces may participate in fiber-to-fiber bond formation. The most important is that of hydrogen bond formation although other bonding forces such as covalent, ionic (electrostatic) and van der Walls forces may also be involved (3).

Several methods in commercial papermaking may increase sheet strength. This may be by furnish modification, for example the inclusion of a higher proportion of long fibers, a reduction in the amount of inert filler, or by the application of strength additives. It may also be achieved by process modification, for example the use of additives, alkaline pH, increased wet pressing, or the application of starch at the size press or in the coater. Refining (beating) is, however, perhaps the most frequently used tool in paper making for increasing tensile and related strength properties. It may not always be appropriate, however, for, in addition to the cost of the electrical energy consumed, refining usually slows down drainage on the paper machine, increases the density of the resulting sheet and decreases its porosity (4). With the loss of bulk, stiffness may also have been impaired, and tearing resistance decreases. The increased bonding also reduces opacity.

Certain chemical additives, when introduced into the stock prior to paper formation, can lower the degree of refining used for generating paper strength, while maintaining other important property combinations. Dry strength additives are usually water soluble, hydrophilic natural and synthetic polymers. Cationic starch and acrylamide polymers are the most commercially important ones. However, many difficulties and inconsistencies were experienced in using modified starches (5). The acrylamide polymers were developed in 1955 for dry strength improvement. For effective performance, however, the anionic acrylamide resin must be fixed on the fiber by alum. The next, in the dry strength improvement area, was the combination of the acrylamide resin and the cationic resin, which is effective only from pH of 4.0 to 7.0 (6). Most of the pulp and paper mills have converted into or are in the process of converting into alkaline papermaking. Sizing of paper in alkaline conditions was a real challenge that has been overcome by the introduction of alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD) sizing, and more work is being done in this area. Commercial dry strength agents can be used at a pH of not more than 7.0 with some exceptions. Thus, there is a need to introduce newer dry strength agents that can be used at higher pH levels. Polyallylamine·HCl is capable of this and can be considered as an exciting dry strength agent. However, the cost benefit of this has to be looked upon.

THEORY AND BACKGROUND

Bonding between fibers is the very essence of dry strength development of paper. Hydrogen bonding between the numerous hydroxyl groups on the surfaces of adjacent cellulose fibers and fibrils in a fiber mat is the primary source of fiber-fiber bonding in dry paper. “Hydrogen bonding occurs when hydrogen that is bonded to one of the four highly electronegative elements (F, O, N, or Cl) comes near a second highly electronegative element” (3). Partial charges develop between the hydrogen and electronegative element since the bond is fairly ionic.

Polyallylamine was found as a suitable mordant for rosin sizing (7). In our laboratory, efforts had been focussed on determining the mechanism of action for mordant based on coordination chemistry and developing new mordants for rosin sizing that would be effective under alkaline conditions (7-10). Sizing in alkaline conditions has been very problematic to the industry. Previous work (7) in this laboratory has shown that among the various polyamines used in the study, polyallylamine was the most effective mordant, even in the alkaline region, and was

extraordinarily more effective than rosin-alum sizing at pH 4.5, which has been the dominant process since the early 1800s. However, its effect as a dry strength additive has not been studied.

The hypothesis here is based on the assumption that amine groups can provide direct anchoring to the fiber and thus increase the fiber-to-fiber bonding. The cationic polyallylamine·HCl can electrostatically bond with the anionic sites on fibers, fines and fillers. Interactions between cationic surfactants (PAA) and polyanionic solid polymers (cellulose and hemicellulose) in aqueous solutions can be described as cooperative binding (11). As a result of this interaction, the cationic polyallylamine·HCl will be in intimate contact with the fiber surface, which will ensure the retention of the chemical on the fiber. There the additional bonding can reinforce the strength of the cellulosic bonds. The strength contribution of polyallylamine·HCl could be the joining together of the fibers and the fines into a cohesive network. The structure of polyallylamine·HCl is shown in **Figure 1**. Five carbon atoms separate the amine groups. It has a long chain of C-C and thus there are more probable sites for hydrogen bonding. Work by Dougherety (12) summarizes cationic-π interactions that form between cations and aromatic structures. The cationic amine can form interactions with the aromatic π-bonding of lignin. The other amino compounds used for the study are ethanolamine·HCl and aminobutyric acid (**Figure 2**). In the case of aminobutyric acid, it was assumed that the amine group will form interactions with lignin and thus the carboxylate end group could form additional hydrogen bonding. Surprisingly, however, the strength properties with these additives were not affected. One reason for this might be the short chain of C-C in these compounds as compared to the long C-C chain in polyallylamine·HCl.

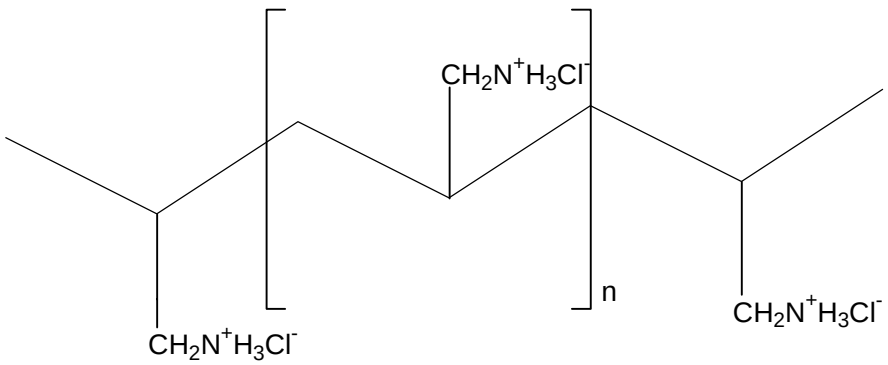
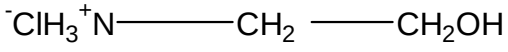


Figure 1. Structure of polyallylamine·HCl.

a.



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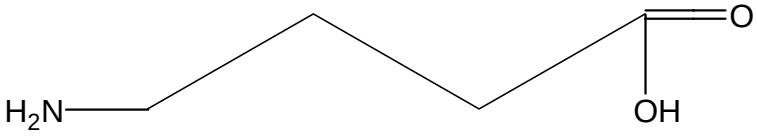

Figure 2. Structures of (a) ethanolamine·HCl, (b) aminobutyric acid.

RESULTS AND DISCUSSION

Dry strength with various pulps

Thermomechanical (TMP) pulp, unbleached kraft softwood (SW) pulp and bleached kraft softwood (SW) pulp were used to make laboratory handsheets using 0.25% to 1.0% polyallylamine·HCl (based on the mass of oven dry pulp) as dry strength agent. The strength properties in these handsheets were compared to control handsheets using 0% additives and 0.5% and 1.0% starch at a pH of 9.0. Some handsheets were air-dried overnight and some were dryer-dried at 250^{o}F for three minutes. The strength properties in the handsheets were determined using the TAPPI standard procedures. The results are shown in the tables.

The different types of treatments and the corresponding strength properties on bleached kraft SW pulp are shown in this **Table 1**. It was observed that there was not a big difference in the strength properties with the addition of ethanolamine·HCl, aminobutyric acid and aminocaproic acid as dry strength additives. Hence, these results will not be discussed in detail. For handsheets made from unbleached kraft SW pulp, and dryer-dried, 0.5% polyallylamine·HCl imparts an increase in the burst, folds and tensile properties (**Table. 2**). The most effect being on the double folds of the handsheets. For handsheets made from bleached kraft SW pulp (Table 1), 1.0-% polyallylamine·HCl was required to obtain similar strength improvement.

For handsheets made from thermomechanical pulp (**Table 3**), with the addition of 1.0-% polyallylamine·HCl, the strength properties increased only to a small extent. Thus, unbleached kraft pulp gives better fiber-fiber bonding with the addition of polyallylamine·HCl.

Treatment	Burst Index kPa.m^2/g		Double Folds		Tear Index mN.m^2/g		Breaking length, km	
	AD[a]	DD[b]	AD	DD	AD	DD	AD	DD
Control	1.9	1.9	22	23	28.4	27.2	3.1	2.9
2% aminobutyric acid	1.9	1.9	27	27	27.5	26.5	3.0	3.3
2% aminocaproic acid	1.6	1.6	24	23	28.1	27.6	2.9	3.0
2% ethanolamine.HCl	2.2	2.1	41	44	28.4	28.9	3.2	3.4
0.5% starch	1.9	1.9	25	25	26.3	26.1	2.9	3.0
1.0% starch	2.2	2.3	42	44	25.6	25.4	3.1	3.2
0.25% PAA[c]	2.5	2.7	50	58	26.8	27.5	5.5	5.7
0.5% PAA	2.9	3.2	91	107	27.8	27.8	5.8	6.7
1.0% PAA	3.7	4.2	250	283	20.9	18.5	6.6	7.2

[a] the handsheets were air-dried overnight.

[b] the handsheets were drier-dried at 250^{o}F for 3 minutes and then conditioned in standard conditions.

[c] polyallylamine·HCl

Table 1. The effect of different chemical additives on the strength properties of bleached kraft SW pulp.

Treatment	Burst Index kPa.m^2/g		Double Folds		Tear Index mN.m^2/g		Breaking length, km	
	AD[a]	DD[b]	AD	DD	AD	DD	AD	DD
Control	1.47	1.70	30.8	52.2	20.23	21.54	2.86	2.92
0.5% PAA[c]	4.24	4.57	871	1132	21.36	20.84	4.16	4.86

[a] the handsheets were air-dried overnight.
[b] the handsheets were drier-dried at 250^{o}F for 3 minutes and then conditioned in standard conditions.
[c] polyallylamine·HCl

Table 2. The effect of addition of PAA on the strength properties of unbleached kraft SW pulp.

Treatment	Burst Index kPa.m2/g		Double folds		Tear Index mN.m2/g		Breaking length, km	
	AD[a]	DD[b]	AD	DD	AD	DD	AD	DD
Control	1.35	1.49	7.2	7.6	13.1	13.2	2.75	2.72
1% starch	1.38	1.44	7.0	8.0	13.4	13.4	2.75	2.83
0.5% PAA[c]	1.30	1.59	7.3	10.4	13.5	13.4	3.33	3.65
1% PAA	1.40	1.99	8.0	16.4	13.4	13.2	3.77	3.98

[a] the handsheets were air-dried overnight.
[b] the handsheets were drier-dried at 250^{o}F for 3 minutes and then conditioned in standard conditions.
[c] polyallylamine·HCl

Table 3. The effect of various chemical additives on the strength properties of thermomechanical pulp.

Effect of the concentration of chemical addition

The effect of the amount of PAA added to the pulp (based on mass of oven dry pulp) on the strength properties is important. It is clear that the increase in the addition of PAA increases the sheet strength. For example, the results in Table 1 show that the double folds for the dryer-dried sheets with 0% additives is 23. The addition of 0.25% PAA increases it to 58, while with further increase in PAA to 0.5%, the double folds increases to 107 and finally with 1.0% PAA it is 283. However, by further increasing the amount of PAA, the sheet formation is adversely affected. Increased flocculation can be one of the causes for this problem. This can generally be overcome by looking at the addition point of the additive and ensuring that thorough mixing takes place after addition. This can break up the flocs and ensure improved formation.

Effect of fiber furnish

The various types of wood pulp fibers used in papermaking affect sheet strength for many different reasons. In our study, we used the thermomechanical pulp, unbleached kraft SW pulp and bleached kraft SW pulp. TMP pulp has a very high lignin content and is produced by mechanical pulping. The unbleached pulp has an intermediate lignin content and the bleached pulp has a very low lignin content. It is observed that the increase in strength properties depend very much on the pulp furnish. We assumed the interactions between the cationic amine and the aromatic π bonding of lignin as well as the interaction between the amine and the cellulose fibers. With TMP pulp, the PAA was not as effective. This indicates that PAA may not be forming hydrogen bonds with the cellulose fibers as much as anchoring to the exposed carboxylate groups of fibers.

Effect of drying condition on dry strength

The drying conditions of the handsheets affected the level of dry strength improvement. Higher levels of dry strength were found in handsheets that were dried in a sheet dryer at 250^{o}F for 3 minutes as compared to the handsheets that were air-dried overnight for sheets made of either TMP, bleached or unbleached kraft pulp. For example, air-dried sheets made with unbleached kraft pulp and 0.5% polyallylamine·HCl gave a burst index of 4.24 kPa.m^2/g; double folds of 871 and breaking length of 4.16 km. In contrast, the corresponding dryer-dried sheets had a burst index of 4.57 kPa.m^2/g; double folds of 1132 and breaking length of 4.86 km (Table-2). The dryer-dried handsheets will have lower moisture content than the air-dried sheets as a result of hysteresis phenomenon (13). It is also possible that a surface activation reaction is occurring (14).

Other factors concerning dry strength

Usually with the increase in burst and tensile strength of paper, the tear resistance decreases. As mentioned earlier, refining increases the burst and tensile strength at the cost of tear strength. With the addition of polyallylamine·HCl, however, the tear strength of the handsheets was not affected for the unbleached kraft pulp and the thermomechanical pulp. For the bleached kraft pulp, the tear strength was not affected at lower levels of addition of polyallylamine·HCl, though at 1.0-% addition of PAA, the tear resistance decreased by almost 20.0%.

The effect of pH value of the pulp stock has not been shown. However, the best results were obtained at a pH of 9.0. The results were not affected and were the same in a pH range of 7.0 to 10.0. Since, the pKa of the protonated amine is approximately 9.0, this material is supposed to give the best results in alkaline conditions.

CONCLUSIONS

Polyallylamine·HCl was shown to be a highly effective dry strength agent for unbleached kraft Douglas-fir pulp at a level of 0.5% addition on pulp. PAA was less effective on unbleached kraft Douglas-fir pulp and even less effective on TMP pulp. The addition of PAA increases the dry strength of paper, notably the folding endurance. The drying conditions of the handsheets affect the strength properties. PAA can provide additional bonding between fiber surfaces where the distance is too great for hydrogen bond formation between adjacent OH groups on cellulose fibers. PAA can be considered an exciting and promising material in the dry strength area of papermaking in some specialized applications.

EXPERIMENTAL PROCEDURES

The unbleached kraft SW pulp had a Canadian Standard Freeness (CSF) of 580 ml. The bleached kraft SW pulp had a CSF of 380 ml. The TMP pulp consisted of over 70% western hemlock. Six grams (air dried basis) of moist pulp was added to 450 ml of water and the slurry was stirred in a food blender for 3 minutes until the stock was well dispersed. The desired amount of the additives was measured and dissolved in water. The solution was then added to the pulp slurry and the mixture was stirred. At this point the pH of the pulp slurry was approximately 7.0. This pH was then adjusted to 9.0 by using NaOH. The slurry was diluted to a consistency of 0.15% using tap water and the pH value was readjusted.

Handsheets of 60-g/m^2 basis weight were made according to TAPPI Test Method 205 sp-95 in the British Sheet Mold using a total water volume in the mold of 5.0 L rather than 7.0 L. The standard press cycle was used, and then the sheets were either dried in the sheet dryer at 250^{o}F for 3 minutes or air dried overnight according to the test method. Dryer-dried sheets were conditioned at 72^{o}F and 50% relative humidity for at least two hours prior to testing. Five to ten handsheets were made under each condition, tested and the results averaged. The bursting strength was determined using the Mullen Bursting Tester according to TAPPI T-403 om-85. The tensile breaking strength, reported as breaking length, was determined according to TAPPI T-404 om-87. The folding endurance was measured using the MIT tester according to TAPPI T-511 om-88. The internal tearing resistance was determined using the Elmendorf-type tester according to TAPPI T-414 om-88.

Cationic starch was obtained from Grain Processing Corporation with a brand name "Chargemaster R430 Cationic Starch." Polyallylamine·HCl with a molecular weight of 70,000 was obtained form Aldrich Chemical Company, Inc., Milwaukee, WI. Ethanolamine·HCl, aminobutyric acid and aminocaproic acid were also obtained from Aldrich Chemical Company, Inc.

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