


AN ABSTRACT OF THE THESIS OF

Mahesh Shrikant Rathi for the degree of Master of Science in Forest Products presented on July 20, 1999.

Title: APPLICATION OF POLYALLYLAMINE AS A DRY STRENGTH AGENT FOR PAPER.

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Abstract approved:


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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·HCl (PAA), 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 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.

APPLICATION OF POLYALLYLAMINE AS A DRY STRENGTH AGENT

FOR PAPER

by

Mahesh Shrikant Rathi

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Mahesh Shrikant Rathi, Author

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Dedicated

to my beloved Dad
and in the loving memory of
my late grandparents.

APPLICATION OF POLYALLYLAMINE AS A DRY STRENGTH AGENT FOR PAPER

1. Introduction

1.1 What is dry strength in paper, and why is it important?

The dry strength of paper is its inherent structural property. The dry strength of paper means different things to different people, depending upon the primary end use for which the product is intended. Thus, the ability of paper to resist bursting stresses (its burst strength) may be the main consideration when discussing the structural properties required for a paper bag. In other applications, paper's resistance to rupture by tensile stress or its ability to resist rupture during repeated folding may be the primary requirement.

1.2 Discussion on dry strength of paper versus its wet strength

Paper is a network of cellulose fibers bonded together in a mat. Each of the fiber-fiber contacts are

held together by intermolecular forces such as hydrogen bonds. These bonds are very sensitive to water; the extent of bonding decreasing steadily as the moisture of paper increases (1).

Paper products must retain some strength when subjected to high humidity or when soaked in water. It is possible to produce paper products with wet strength in the range of 20-40% of the dry strength by using some wet strength additives. The papers are classified as wet strength papers if their wet breaking length is at least 15-20% of their dry breaking length (2). In this report, however, only dry strength of paper will be considered in detail.

1.3 Concepts of fiber-fiber bonding

It may seem astonishing that a suspension of wood pulp fibers in water, screened to form a wet mat, can then be de-watered by three simple processes, drainage, wet-pressing and evaporation, to form a fibrous structure having considerable strength. An extensive research effort has been devoted to understand the mechanisms by which dry strength is developed.

The bonding between the fibers is the very heart of dry strength development of paper. A mass of short fibers that remains unbounded does not produce a sheet of paper having either structural integrity or strength. Given a reasonably strong fiber furnish, at least moderate bonding between these fibers must be developed to produce a reasonably strong paper.

To explain and control the development of dry strength in paper we will discuss both the nature and the origin of fiber-to-fiber bonds. The following types of bonding are at least theoretically possible and most have been proposed at one time or another.

1. Mechanical entanglement of fibers or surface fibrils.
2. Covalent bonding.
3. Ionic bonding.
4. Hydrogen bonding.
5. Bonding by van der Waals forces.

1.3.1 Mechanical entanglement of fibers

It was thought that mechanical entanglement accounts for most or all of the fiber-to-fiber bonding in a dry sheet of paper (3). The interweaving of the

fibers within a complex fibrous mat would be adequate to account for considerable dry strength development, however the virtual absence of this process has been demonstrated (4). Paper is not basically an interwoven fibrous mat. Alternatively, mechanical entanglement could involve the many fibrils on the surfaces of beaten pulp fibers. However, most research workers do not accept this viewpoint. The electron micrography evidence of Jayme and Hunger (5) clearly demonstrates strands consisting of microfibril bundles and remnants of beaten fiber outer walls spanning between adjacent fibers in paper, but this type of fiber-to-fiber bonding does not represent mechanical entanglement.

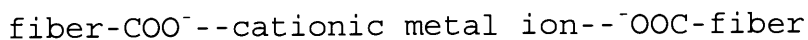
1.3.2 Covalent bonding

Paper essentially loses all of its strength (i.e., has no wet strength) when immersed in water. Covalent bonding (50-100 Kcal/mole), presented as the second in the above list of possibilities, has been proposed in attempts to explain the wet strength which is imparted to paper by the addition of various wet strength additives (6). Wet strength improvement sometimes tends

to be accompanied by an equal increase in dry strength, so it has been suggested that the increased dry strength is also the result of covalent fiber-resin-fiber bonding (7). However, covalent bonding as an appreciable source of bonding between fibers has not been advanced because it would be difficult to explain the reason for a covalently bonded structure to readily lose its dry strength by simple immersion in water at room temperature.

1.3.3 Ionic bonding

Ionic bonds (10-30 Kcal/mole), next to covalent bonding, could account for strong fiber-to-fiber bonding which would nevertheless be completely disrupted by water. Further, carboxyl groups in wood pulp fibers could conceivably lead to a considerable amount of ionic bonding. With the assistance of metal ions in the aqueous phase, the development of ionic bonds of the following type can take place (8).



Calcium or aluminum would be the most likely metals to participate in these ionic bonds. The concept

that ionic bonding is the chief source of fiber-to-fiber bond development in untreated paper has not been thought important by paper scientists, probably for lack of specific evidence. However, work involving surface modified fibers in which certain sheet strength improvements are cited to demonstrate the development of considerable ionic bonding between these specially treated fibers has been reported (9).

1.3.4 Hydrogen bonding

During the last several years, most paper scientists have accepted the concept that hydrogen bonding (4-6 Kcal/mole) between the vast number of hydroxyl groups on the surfaces of adjacent cellulose fibers and fibrils in a fiber mat is the primary source of fiber-to-fiber bonding in dry paper. Let us discuss the logic supporting the concept of hydrogen bonding between cellulose fibers. First, the potential bonding material, the cellulose hydroxyl groups, is readily available on the surfaces of hydrated wood pulp fiber (10). In fact, it is almost universally agreed that the hydration (intimate association of water molecules with

cellulose) of these fiber surfaces represents profuse hydrogen bonding between water molecules and surface hydroxyl groups. It seems rather simple for this hydrogen bonding to be transferred into hydrogen bonding between the hydroxyl groups of adjacent fiber surfaces as the latter are brought into very intimate contact during the simultaneous removal of the water molecules from a wet fiber mat. This suggested mechanism for the development of fiber-fiber bonding is illustrated in figure 1.1.

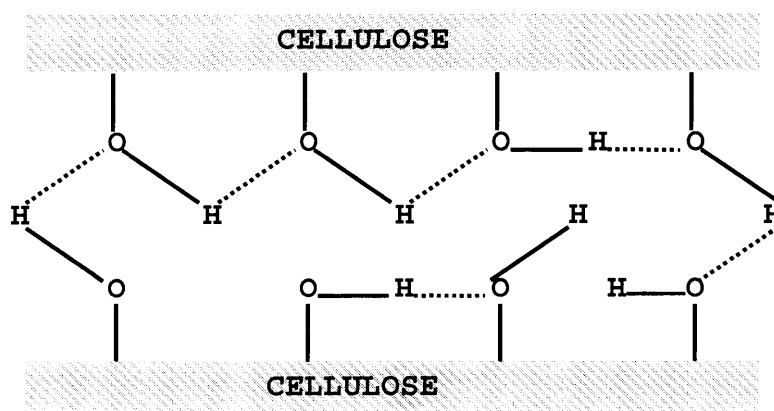


Figure 1.1 Hydrogen bonding between adjacent fibers.

When a wet fiber mat is formed, pressed, and dried, adjacent fibers come into close contact with each other and interfiber hydrogen bonding can be

developed between cellulose surfaces as the water molecules are removed. Thus, figure 1.1 shows two adjacent fibers that have become hydrogen bonded while being dried. Secondly, it has been emphasized for years that the primary source of the great strength of cellulose fibers themselves, is the massive hydrogen bonding between the hydroxyl groups of adjacent cellulose polymer chains (11). If hydrogen bonding accounts for the tremendous tensile strength of cellulose fibers, it would seem that this process would also provide the relatively limited bond strength between fibers in paper.

The scientific evidence that has been combined to support hydrogen bonds as the main source of bonding between fibers is quite convincing, even though it does not involve direct critical experiments. It has been demonstrated that wet pieces of smooth cellophane film become well bonded if they are dried while being held in close surface contact (12). This observation would seem to rule out the mechanical entanglement mechanism in favor of such a chemical bonding process as hydrogen bonding. Various publications (13-14) have reported that the formation of a wet fiber mat from an aqueous

slurry, followed by the solvent-exchange replacement of the water by a series of liquids of decreasing polarity and then by drying, produces a relatively weak sheet of paper. Thus, the presence of water or some other highly polar liquid capable of hydrogen bonding seems required for the development of good dry strength in paper. A similar experimental approach involved the freeze-drying of a fiber mat formed from aqueous slurry, followed by sublimation to remove the water from the sheet (14-15). The resulting dry paper was very weak, presumably because the absence of liquid water during the de-watering of the wet mat prevented the development of inter-fiber hydrogen bonding. Infrared analysis indicated that most of the hydroxyl groups of the isolated fibers were involved in intra-fiber hydrogen bonding. This experimental result is often cited as convincing proof of the existence of inter-fiber hydrogen bonding in paper (16).

1.3.5 Bonding by van der Waals forces

Some skeptics feel that the case for hydrogen bonds as the main source of fiber-to-fiber bonding has

yet to be proved. It can be argued that the imposition or assumption of hydrogen bonding is not necessary, because the ever present van der Waals forces (0.5-2 Kcal/mole) are sufficient to account for the bonding between adjacent fibers which are in very close large-area contact. Since any two surfaces stick together to some extent if they are in very close contact (i.e., approach within a few Angstrom units), it seems that this should be the case for paper fibers in a tightly consolidated dry web. The amount of close bonding contact between two adjacent fibers in a sheet of paper is another area of considerable scientific disagreement. However, a very weak type of bonding spread over a large area of contact should provide the required amount of bonding between two fibers just as easily as stronger bonds over a much smaller contact area.

To summarize, the specific nature of fiber-to-fiber bonding is still somewhat uncertain. Generally, mechanical entanglement, covalent bonding, and ionic bonds appear to play little or no part. Hydrogen bonding is a plausible and adequate mechanism. However, van der Waals forces offer another possibility, which

cannot be completely ignored. These latter forces could provide weak bonding between all parts of adjacent cellulose molecules and not merely between their polar hydroxyl groups.

1.4 Refining versus strength additives

Refining or beating is the most common means of increasing the dry strength of a paper or board. In the process of refining, energy is applied to the papermaking fibers, which fibrillates them. This creates small tiny fibrils that are attached to the side of the fiber and releases hemicellulose. Hemicellulose is composed of relatively short chain polymers of different types of sugar, and contributes significantly to the dry strength in the paper (17). The extent of the degree of fibrillation depends on the type of pulp as well as the type of refiner used. The pulp will retain more and more water as the degree of refining increases and the fibers will conform more and more to each other resulting in a denser sheet. This in turn reduces the sheet bulk.

Farley (18) reported the changes in the sheet properties that occur when a bleached softwood pulp is refined in a laboratory beater. He found that there were increases in internal bond, burst, folds, and tensile strength of handsheets but these were accompanied by losses in caliper and opacity. Also, the effect of refiners will adversely affect the tear strength due to the shortening of the fiber length.

Dry strength additives are used in order to increase the dry strength without the concomitant losses in caliper, opacity and tear strength.

1.5 Commercial dry strength additives

The main purpose of dry strength additives is to improve the degree of fiber-to-fiber bonding in paper. Dry strength additives are hydrophilic water-soluble polymers that are added to the aqueous pulp slurry. The primary dry strength additives used commercially in the industry are materials such as starches (natural and modified), various natural gums and synthetic polymers.

1.5.1 Cationic starch

Starch is one of the oldest and still most commonly used adhesives today for improving fiber bonding in paper. Other than its role as dry strength agent, it is found useful as a retention aid, surface sizing agent, coating binder and adhesive. In the past unmodified or native starches were used in papermaking to large extents. However, because of their many disadvantages (19), they are not used to any great extent.

Cationic starch contains tertiary amines or quaternary amine salts on 3-5 per 100 anhydroglucose units of starch (20). Figure 1.2 shows the structure of quaternary cationic starch. Moeller (21) proposed that the adsorption of cationic starch creates new bonding sites on the fiber surface, which are stronger than the original fiber-to-fiber bonds. Since the cellulose fibers are usually anionic in nature, the cationic starch is firmly attached to the fiber surface. Retention of cationic starch is possible due to the ionic interaction between the cellulose-COOH groups and the cationic polymer (22). Such an interaction has been

demonstrated between cationic starch and cellulose (23). Cationic starch increases the tensile strength of paper by increasing the bond strength per unit of optically bonded area, and not by increasing the relative bonded area.

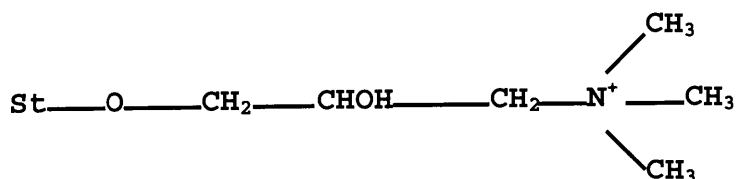


Figure 1.2 Structure of a cationic starch.

1.5.2 Polyacrylamide resins

The most common types of synthetic dry strength additives are based on polyacrylamide. One reason for this is their relatively low cost. Polyacrylamide is essentially a linear non-ionic polymer and its structure can be written as shown in figure 1.3.

Polyacrylamide resins increase the dry strength of paper by hydrogen bonding. The polymer molecule must be long enough to ensure effective adsorption and to provide multiple sites for hydrogen bonding (24).

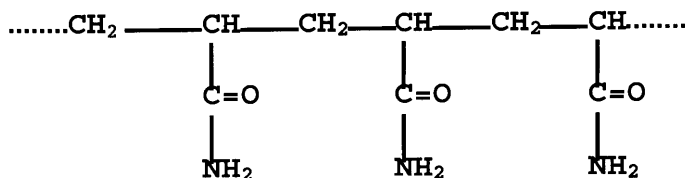


Figure 1.3 Structure of a polyacrylamide.

Polyacrylamides are widely used in the industry today. They can be used over a wide pH range, alum is not required, and can be adapted to all kinds of furnishes. They can also function as retention aids and assist in drainage.

1.6 Paper properties and measurement

The purposes of measuring the dry strength of paper in the laboratory are to predict whether the product will meet the customers' specifications and to make sure that the product will satisfactorily perform the purpose for which it is made.

There are a wide variety of tests and methods employed by papermakers; however, some common methods are selected for various grades of paper products. The common strength properties of paper are:

1. tensile strength

2. toughness
3. bursting strength
4. folding endurance
5. stiffness
6. surface pick resistance
7. tear resistance
8. bending flexibility
9. abrasion resistance

Most of these strength properties are increased by additional bonding between the fibers in a sheet. Transverse tensile strength and resistance to delamination are particularly dependent upon the degree of interfiber bonding. Additional fiber-to-fiber bonding throughout the sheet tends to increase surface strength properties such as abrasion resistance and pick resistance because these require strong bonding of the surface fibers. However, increased fiber-to-fiber bonding usually impairs a few strength properties like tear resistance. The papermaker must resolve this conflict between the two groups of strength properties to achieve an optimum balance for the particular intended use. The following are descriptions of some

methods that are commonly used for dry strength measurement of paper.

1.6.1 Bursting strength (25)

The bursting strength is sometimes also referred as Mullen or pop strength. The Mullen tester is shown in figure 1.4, inserts show the test area. The handsheet (test specimen) is held between the annular clamps and is subjected to an increasing pressure by a rubber diaphragm beneath it. This rubber diaphragm is expanded by hydraulic pressure at a controlled constant rate until the test specimen ruptures. The pressure reading at this stage is recorded as the bursting strength in psi or kPa.

The bursting strength is sometimes also reported as burst factor, burst index or burst ratio. Bursting strength is used as a measure of resistance of paper to rupture. This test is relatively easy and inexpensive.

$$\text{Burst Index} = \text{kPa} / (\text{g/m}^2)$$

$$\text{Burst Factor} = (\text{g/cm}^2) / (\text{g/m}^2)$$

$$\text{Burst Ratio} = \text{psi} / (\text{lb./ream})$$

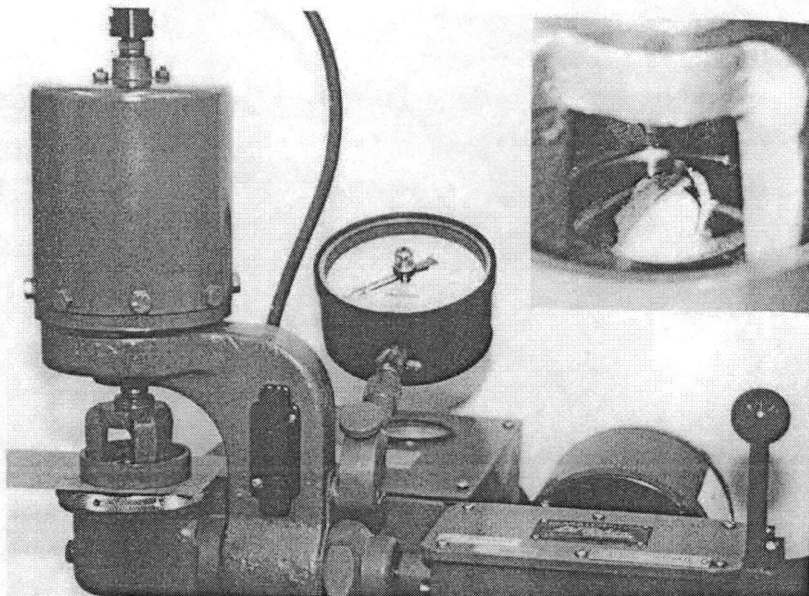


Figure 1.4 Mullen bursting tester (20).

1.6.2 Tensile strength (26)

The tensile strength is shown in figure 1.5. Tensile strength of paper can be defined as the maximum tensile force per unit width developed in the test sample at rupture or break. It is the force per unit width of the specimen. The paper sample is cut into strips that are 20 cm long and 15-25 mm wide. The ultimate force is reported in lb./in, kg/m, or N/m. The tensile strength can alternatively be reported as tensile index and breaking length.

Breaking length of paper (reported in km) is the hypothetical length of paper that just supports its own weight when supported at one end. It is the most common means of reporting tensile strength. It compares the tensile strength regardless to paper thickness, density or width.

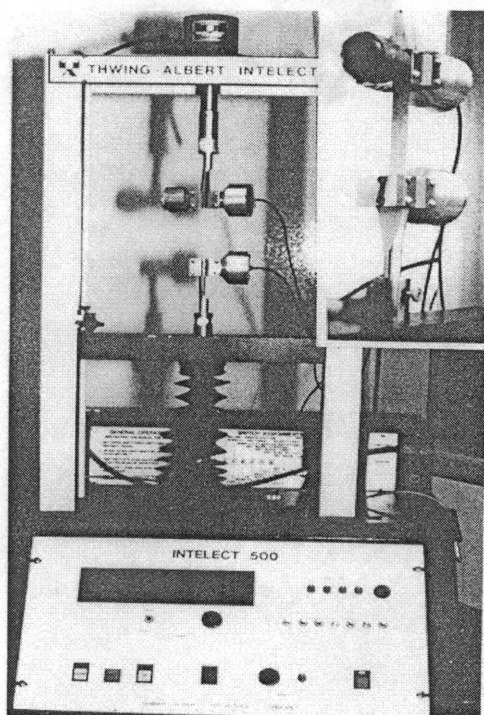


Figure 1.5 Tensile tester (20).

The significance of this test is to indicate the serviceability of many papers that are subjected to direct tensile forces.

1.6.3 Folding endurance (27)

Folding endurance is the measure of the number of double folds required to break the paper when a strip of paper 15mm wide is tested under a standard tension of 9.81 N. The MIT fold tester is shown in figure 1.6.

The test specimen is clamped between the stationary and the oscillating jaws under a force of 9.81 N. When the test is started, the counter starts registering the number of double folds required to break the specimen and stops automatically when the specimen breaks. The reading on the counter is reported as double folds.

The significance of this test is to estimate the ability of paper to withstand repeated bending, folding and creasing. It is also useful for measuring deterioration of paper upon aging. This method is very susceptible to small errors in adjustment and calibration of the instrument and in the relative humidity of the test room.

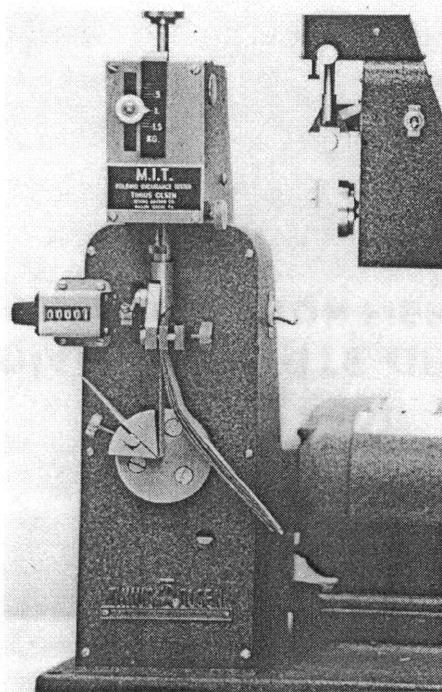


Figure 1.6 MIT folding tester (20).

1.6.4 Tearing resistance (28)

Tearing resistance is a measure of the force perpendicular to the plane of the paper that is required to tear the multiple sheets of paper through a fixed distance after the tear has been already started. Figure 1.7 shows the Elmendorf-type tearing tester.

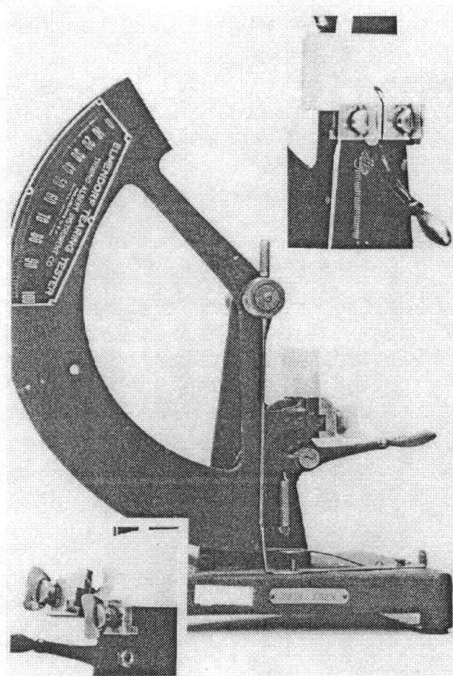


Figure 1.7 Elmendorf-type tear tester (20).

The work done in tearing the sheets is measured by the loss of potential energy of the pendulum. The average force exerted when a certain number of sheets are torn together is indicated by the calibrated instrument scale. Certain numbers of sheets are clamped in the two jaws. The initial cut is given with a knife blade. The value is reported in g.cm/sheet. There are numerous other tests of paper covered in the TAPPI Standard and other standards.

1.7 Research interests in the dry strength area

Papermakers and scientists who are working on the dry strength and wet strength area of papermaking have put most of their efforts on the following:

1. Searching for new chemicals and strategies that could introduce more effective dry and wet strength while maintaining other favorable properties of paper.
2. Understanding the existing mechanisms of strength development of paper so that they might be used more effectively.
3. Modifying existing systems of strength development to improve their performance.
4. Studying the chemistry between the vast number of chemical additives, that can be used as strength improving agents, and the cellulose fibers.

This thesis concentrates on the development of new dry strength agents.

1.8 Literature cited

1. Britt, K.A. 1965. Introduction. In Wet Strength in Paper and Paperboard, ed. J. Weidner, 1-8. Technical Association of Pulp and Paper Industry, New York.
2. Britt, K.W. 1948. Review of development in wet strength paper. Technical Association Papers, 594-596. Tappi Press, NY.
3. Wilson, W.S. 1951. The Mechanism of Fiber Bonding. TAPPI 34(12):561-566.
4. Bolam, F. 1966. Consolidation of the paper web. 189-214. BPBMA, London.
5. Jayme and Hunger. 1962. Electron Microscope 2- and 3-dimensional classification of fiber bonding. In Formation and Structure of Paper, ed. F. Bolam, 135-170. BPBMA, London.
6. Landes, C.G. 1950. The resin bonding of paper fibers. TAPPI 33(9):463-471.
7. Church, S., Jurecic, A., Lindh, T. and Stannett, V. 1958. Studies on the mechanism of wet-strength development. TAPPI 41(9):465-468.
8. Davidson, R. 1980. Theory of dry strength development. In Dry Strength Additives, ed. W. F. Reynolds, 1-32. Technical Association of Pulp and Paper Industry, Atlanta.
9. Reif, W.M. 1972. The utilization of ionic bonds in development of paper strength. 47-61. TAPPI Papermakers Conference, Atlanta.
10. Nevell, T.P. and Zeronian, S.H. 1985. Cellulose Chemistry Fundamentals. In Cellulose chemistry and its applications, ed. T.P. Nevell and S.H. Zeronian, 15-29. Ellis Horwood Ltd., West Sussex, England.

11. Clark, G.L. 1930. Cellulose as it is completely revealed by X-rays. Industrial and Engineering Chemistry 22(5):474-487.
12. Clark, J. 1933. The effects of beating on cellulose fibers. Paper Trade Journal 97(26):25-31.
13. Cottrall, L.G. 1950. The influence of hemicelluloses in wood pulp fibers on their papermaking properties. TAPPI 33(9):471-480.
14. Broughton, G. and Wang, J. 1955. The mechanical properties of paper-part III. TAPPI 38(7):412-415.
15. Van Den Akker, J.A. 1952. A note on the theory of fiber-fiber bonding in paper; the influence on paper strength of drying by sublimation. TAPPI 35(1):13-15.
16. Dodson, C.T.J. 1970. The nature of bonds in paper and the behaviour of paper under mechanical strain. Reports on Progress in Physics 33(1):1-43.
17. Fineman, M.N. 1952. The role of the hemicelluloses in the mechanism of wet strength. TAPPI 35(7):320-324.
18. Farley, C.E. 1988. Polyacrylamide dry strength resin applications. In TAPPI wet and dry strength short course, TAPPI, Atlanta.
19. Swanson, J.W. 1956. Beater adhesives and fiber bonding-the need for future research. TAPPI 39(5):257-67.
20. Biermann, C.J. 1996. Handbook of pulping and papermaking, 2nd edition. Academic Press, San Diego.
21. Moeller, H.W. 1966. Cationic starch as a wet-end strength additive. TAPPI 49(5):211-214.
22. Swanson, J.W. 1961. The science of chemical additives in papermaking. TAPPI 44(1):142A-181A.

23. Marton, J. and Marton, T. 1976. Wet-end starch: adsorption of starch on cellulosic fibers. TAPPI 59(12):121-124.
24. Reynolds, W.F. and Wasser, R.B. 1981. Dry-strength resins. In Pulp and Paper, Chemistry and chemical technology, ed. J.P. Casey, 1447-1474. John Wiley & Sons, Inc., New York.
25. Bursting strength of paper. 1991. TAPPI Test Methods. Volume I. T 403 om-85.
26. Tensile breaking properties of paper and paperboard (using constant rate of elongation). 1991 TAPPI Test Methods. Volume I. T 494 om-88.
27. Folding endurance of paper (MIT tester). 1991. TAPPI Test Methods. Volume I. T 511 om-88.
28. Internal tearing resistance of paper (Elmendorf-type method). 1991. TAPPI Test Methods. T 414 om-88.

APPLICATION OF POLYALLYLAMINE AS A DRY STRENGTH AGENT FOR PAPER

2.1 Introduction

Paper is essentially a laminated structure composed of cellulose fibers and bonds between these fibers. Paper has been described as a bonded fibrous network, which may consist only of cellulose, air and water (1). The air within and between fibers contributes nothing to the structure's strength properties. Water, in the form of moisture held by the fibers and bonds, often has considerable influence on the strength of paper. With this exception, however, the dry strength of a paper structure depends only upon its fibers, fiber-to-fiber bonds, and the distribution of these two elements.

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) (2). Fiber-to-fiber bonds are usually weaker than the strength of individual fibers until the latter becomes the limiting factor in a well-bonded sheet (3). 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.

Mechanical entanglement leading to fiber flocculation is a 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 Waals forces may also be involved (4).

There are several methods in commercial papermaking to 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 (5). 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 commercially the most important ones. However, many difficulties and inconsistencies were experienced in using modified starches (6). The acrylamide polymers were developed in 1955 for dry strength improvement. However, for effective performance, the anionic

acrylamide resin must be fixed on the fiber by alum. The next was the combination of the acrylamide resin and the cationic resin, which is effective only from pH of 4.0 to 7.0 (7). 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 and it 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. The 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, which can be used at higher pH levels. Polyallylamine·HCl is capable of this and can be considered as an exciting dry strength agent.

2.2 Theory and background

Bonding between fibers is the very essence of dry strength development of paper. Hydrogen bonding (shown in figure 1.1) 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" (4). Partial charges develop between the hydrogen and electronegative element since the bond is fairly ionic.

As shown in the figure 1.1, when hydrogen that is bonded to a highly electronegative element, in this case oxygen, comes near a second highly electronegative element, again oxygen, hydrogen bonding occurs. The dashed lines show the hydrogen bonds.

Polyallylamine·HCl was found as a suitable mordant for rosin sizing (8). 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 (8-11). Sizing in alkaline conditions has been very problematic to the industry. Previous work (8) in this laboratory has shown that among the various polyamines used in the study, polyallylamine·HCl 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, their effect as dry strength additives 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 (12).

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 2.1.

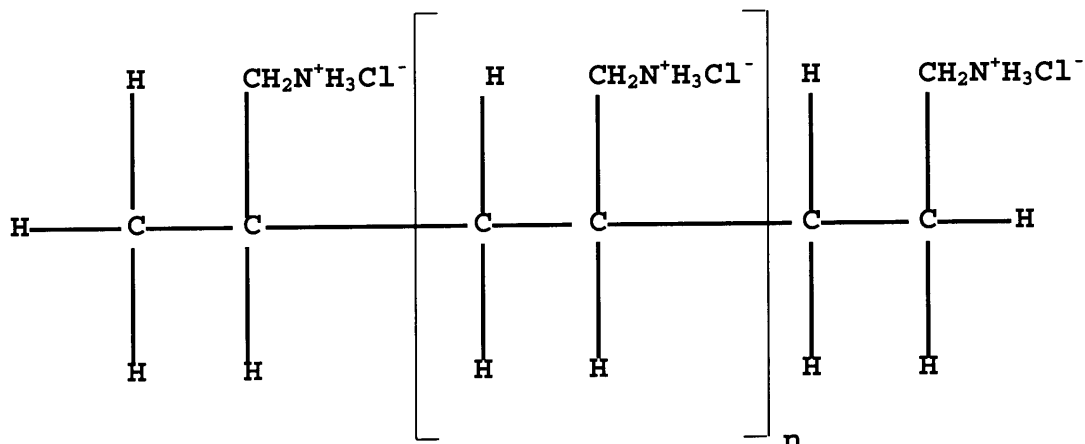


Figure 2.1 Structure of polyallylamine·HCl.

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 Dougherty (13) 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 polyamines used for the study are ethanolamine·HCl and aminobutyric acid. Their structures are shown in figure 2.2. In the case of aminobutyric acid, it was assumed that the amine group will form interactions with lignin and thus the carboxylate end

group can 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.

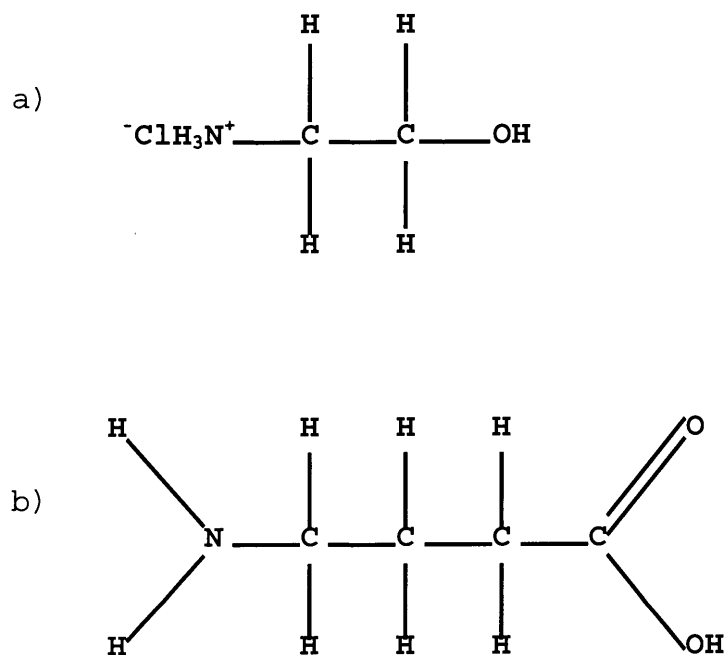


Figure 2.2 Structures of (a) ethanolamine·HCl, (b) aminobutyric acid.

2.3 Results and discussion

2.3.1 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 (AD) overnight and some were dryer-dried (DD) at 250°F for three minutes. The strength properties in the handsheets were determined using the TAPPI standard procedures. The results are shown in the tables.

Table 2.1 shows the results obtained on bleached kraft SW pulp. The different types of treatments and the corresponding strength properties are shown in this table. From the table, we can see 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.

Table 2.1 The effect of different chemical additives on the strength properties of bleached kraft SW pulp.

Treatment	Burst Inde		Double		Tear Index Breaking			
	kPa.m ² /g		Folds		mN.m ² /g 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 ^c	2.9	3.2	91	107	27.8	27.8	5.8	6.7
1.0% PAA ^c	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°F for 3 minutes and then conditioned in standard conditions.

^c polyallylamine.HCl

Table 2.2 The effect of addition of PAA on the strength properties of unbleached 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

Table 2.3 The effect of various chemical additives on the strength properties of thermomechanical 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	1.35	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 ^c	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°F for 3 minutes and then conditioned in standard conditions.

^c polyallylamine·HCl

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. 2.2). The most effect being on the double folds of the handsheets. For handsheets made from bleached kraft SW pulp (Table 2.1), 1.0% polyallylamine·HCl was required to obtain similar strength improvement. For handsheets made from thermomechanical pulp (Table 2.3), with the addition of 1.0% polyallylamine·HCl, the strength properties increased to quite a small extent. Thus, unbleached kraft pulp gives better fiber-fiber bonding with the addition of polyallylamine·HCl.

2.3.2 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 shown in Figure 2.3. It is clear that the increase in the addition of PAA increases the sheet strength.

From the graph we can see that the double folds for the dryer-dried sheets with 0% additives is 23. With the addition of 0.25% PAA it increases 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, with further increase in the amount of PAA added, the sheet formation is adversely affected. Increased flocculation can be one of the causes for this problem. This can be generally 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.

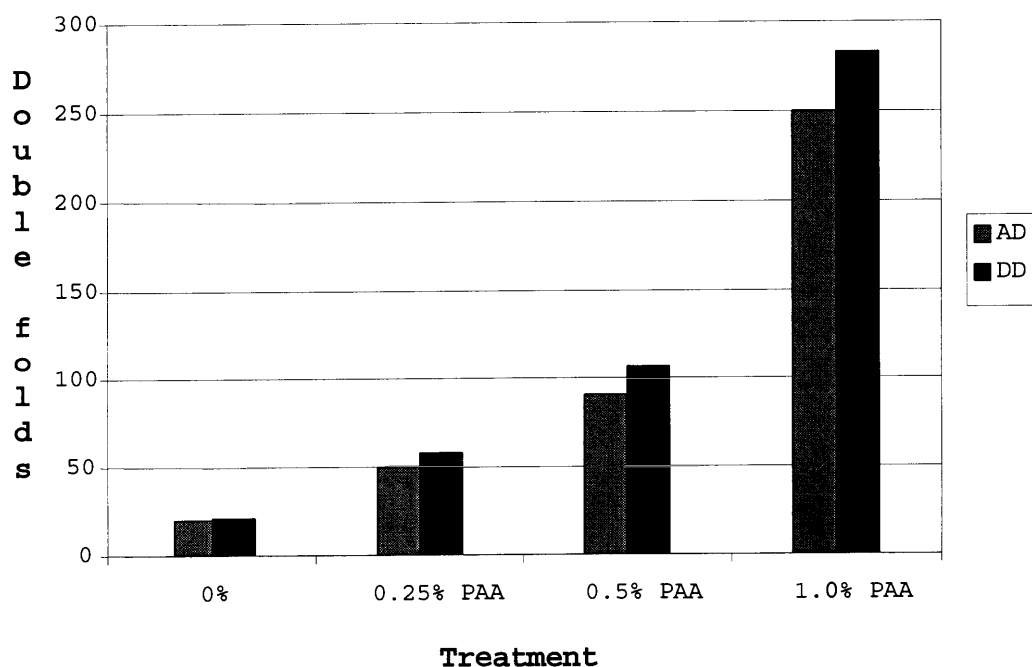


Figure 2.3 The effect of increasing concentration of PAA on double folds of the bleached kraft SW pulp.

2.3.3 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 it is produced by mechanical pulping. The unbleached pulp has an intermediate lignin content and the bleached pulp has a very low lignin content.

Figure 2.4 shows the effect of 0.5% PAA addition on the bursting strength of different types of pulps. From this graph and the earlier discussion, it is clear 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.

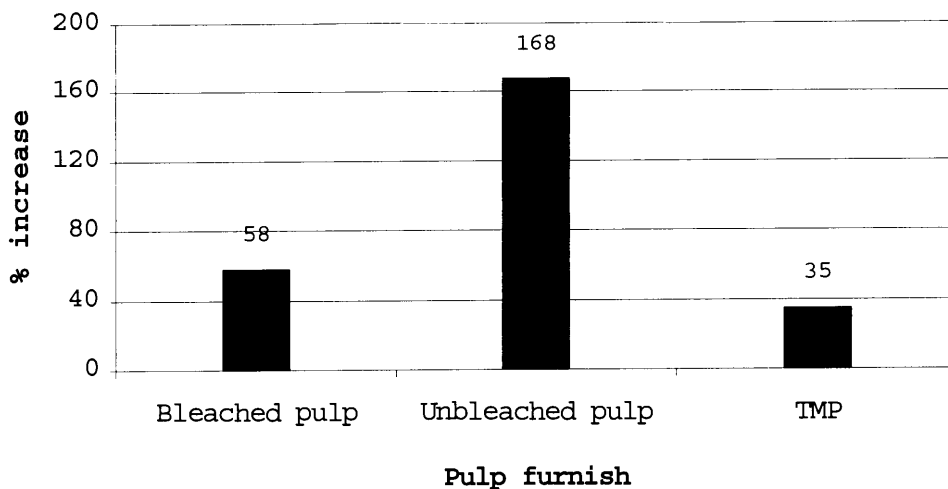


Figure 2.4 % increase in bursting strength of different types of pulps with the addition of 0.5 % PAA

2.3.4 Effect of heating treatment 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°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 burst index of 4.24 kPa.m²/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.m²/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 (14). It is also possible that a surface activation reaction is occurring (15).

2.3.5 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 affect 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.

2.4 Conclusions

Polyallylamine·HCl was shown to be 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 bleached kraft Douglas-fir pulp as compared to unbleached kraft pulp and still further 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 a promising material in the dry strength area of papermaking in some specialized applications.

2.5 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 were 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/m² 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°F for 3 minutes or air dried overnight according to the test method. Dryer-dried

sheets were conditioned at 72°F and 50% relative humidity for at least 2 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 from Aldrich Chemical Company, Inc., Milwaukee, WI. Ethanolamine·HCl, aminobutyric acid and aminocaproic acid were also obtained from Aldrich Chemical Company, Inc.

2.6 Literature cited

1. Dodson, C.T.J. 1970. The nature of bonds in paper and the behaviour of paper under mechanical strain. Reports on Progress in Physics 33(1):1-43.
2. Leech, H.J. 1954. An investigation of the reasons for increase in paper strength when locust bean gum is used as a beater adhesive. TAPPI 37(8):343-349.
3. Page, D.H. 1969. A Theory for the Tensile Strength of Paper. TAPPI 52(4):674-681.
4. Biermann, C.J. 1996. Handbook of pulping and papermaking, Academic Press, San Diego.
5. Marton, J. 1996. Dry strength additives. In Paper Chemistry, 2nd edition, ed. J.C. Roberts, 83-97. Blackie Academic & Professional, Glasgow, New Zealand.
6. Swanson, J.W. 1956. Beater adhesives and fiber bonding-the need for future research. TAPPI 39(5):257-267.
7. Reynolds, W.F. 1980. Acrylamide-based polymers for dry strength improvement of paper. In Dry strength additives, ed. W.F. Reynolds, 125-148. TAPPI Press, Atlanta.
8. Biermann, C.J. 1992. Rosin sizing with polyamine mordants from pH 3 to 10. TAPPI 75(5):166-171.
9. Zhuang, J. and Biermann, C.J. 1995. Neutral to alkaline rosin soap sizing with metal ions and polyethylenimine as mordants. TAPPI 78(4):155-162.
10. Chen, M. and Biermann, C.J. 1995. Investigating of the mechanism of paper sizing through a desizing approach. TAPPI 78(8):120-126.
11. Jing, Q. and Biermann, C.J. 1998. Octadecylamine as an internal sizing agent. TAPPI 81(4):193-197.

12. Hayakawa K. and Kwak, J. 1991. Interactions between polymers and cationic surfactants. In Cationic Surfactants: Physical Chemistry, ed. D.N. Rubingh and P.M. Holland, 240-241. Marcel Dekker, Inc., NY.
13. Dougherty, D.A. 1996. Cationic- π interactions in chemistry and biology: A new view of Benzene, Phe, Tyr, and Trp. *Science* 271(1):163-167.
14. Stamm, A.J. 1964. Wood and Cellulose Science. Ronald Press Co., NY, 145-148.
15. Chen, M, Zhunag, J. and Biermann, C.J. 1997. Rosin soap sizing without mordants by immersion in size solution. *TAPPI* 80(1):271-276.

Bibliography

Biermann, C.J. 1992. Rosin sizing with polyamine mordants from pH 3 to 10. TAPPI 75(5):166-171.

Biermann, C.J. 1996. Handbook of pulping and papermaking, 2nd edition. Academic Press, San Diego.

Bolam, F. 1966. Consolidation of the paper web. 189-214. BPBMA, London.

Britt, K.A. 1965. Introduction. In Wet Strength in Paper and Paperboard, ed. J. Weidner, 1-8. Technical Association of Pulp and Paper Industry, New York.

Britt, K.W. 1948. Review of development in wet strength paper. Technical Association Papers, 594-596. Tappi Press, New York.

Broughton, G. and Wang, J. 1955. The mechanical properties of paper-part III. TAPPI 38(7):412-415.

Chen, M. and Biermann, C.J. 1995. Investigating of the mechanism of paper sizing through a desizing approach. TAPPI 78(8):120-126.

Chen, M; Zhunag, J. and Biermann, C.J. 1997. Rosin soap sizing without mordants by immersion in size solution. TAPPI 80(1):271-276.

Church, S., Jurecic, A., Lindh, T. and Stannett, V. 1958. Studies on the mechanism of wet-strength development. TAPPI 41(9):465-468.

Clark, J. 1933. The effects of beating on cellulose fibers. Paper Trade Journal 97(26):25-31.

Clark, G.L. 1930. Cellulose as it is completely revealed by X-rays. Industrial and Engineering Chemistry 22(5):474-487.

Cottrall, L.G. 1950. The influence of hemicelluloses in wood pulp fibers on their papermaking properties. TAPPI 33(9):471-480.

Davidson, R. 1980. Theory of dry strength development. In Dry Strength Additives, ed. W. F. Reynolds, 1-32. Technical Association of Pulp and Paper Industry, Atlanta.

Dodson, C.T.J. 1970. The nature of bonds in paper and the behaviour of paper under mechanical strain. Reports on Progress in Physics 33(1):1-43.

Dougherty, D.A. 1996. Cationic- π interactions in chemistry and biology: A new view of Benzene, Phe, Tyr, and Trp. Science 271(1):163-167.

Farley, C.E. 1988. Polyacrylamide dry strength resin applications. In TAPPI wet and dry strength short course, TAPPI, Atlanta.

Fineman, M.N. 1952. The role of the hemicelluloses in the mechanism of wet strength. TAPPI 35(7):320-324.

Hayakawa K. and Kwak, J. 1991. Interactions between polymers and cationic surfactants. In Cationic Surfactants: Physical Chemistry, ed. D.N. Rubingh and P.M. Holland, 240-241. Marcel Dekker, Inc., NY.

Jayne and Hunger. 1962. Electron Microscope 2- and 3-dimensional classification of fiber bonding. In Formation and Structure of Paper, ed. F. Bolam, 135-170. BPBMA, London.

Jing, Q. and Biermann, C.J. 1998. Octadecylamine as an internal sizing agent. 81(4):193-197.

Landes, C.G. 1950. The resin bonding of paper fibers. TAPPI 33(9):463-471.

Leech, H.J. 1954. An investigation of the reasons for increase in paper strength when locust bean gum is used as a beater adhesive. TAPPI 37(8):343-349.

Marton, J. 1996. Dry strength additives. In Paper Chemistry, 2nd edition, ed. J.C. Roberts, 83-97. Blackie Academic & Professional, Glasgow, New Zealand.

Marton, J. and Marton, T. 1976. Wet-end starch: adsorption of starch on cellulosic fibers. TAPPI 59(12):121-124.

Moeller, H.W. 1966. Cationic starch as a wet-end strength additive. TAPPI 49(5):211-214.

Nevell, T.P. and Zeronian, S.H. 1985. Cellulose Chemistry Fundamentals. In Cellulose chemistry and its applications, ed. T.P. Nevell and S.H. Zeronian, 15-29. Ellis Horwood Ltd., West Sussex, England.

Page, D.H. 1969. A Theory for the Tensile Strength of Paper. TAPPI 52(4):674-681.

Reif, W.M. 1972. The utilization of ionic bonds in development of paper strength. 47-61. TAPPI Papermakers Conference, Atlanta.

Reynolds, W.F. 1980. Acrylamide-based polymers for dry strength improvement of paper. In Dry strength additives, ed. W.F. Reynolds, 125-148. TAPPI Press, Atlanta.

Reynolds, W.F. and Wasser, R.B. 1981. Dry-strength resins. In Pulp and Paper, Chemistry and chemical technology, ed. J.P. Casey, 1447-1474. John Wiley & Sons, Inc., NY.

Stamm, A.J. 1964. Wood and Cellulose Science. Ronald Press Co., NY, 145-148.

Swanson, J.W. 1956. Beater adhesives and fiber bonding-the need for future research. TAPPI 39(5):257-267.

Swanson, J.W. 1961. The science of chemical additives in papermaking. TAPPI 44(1):142A-181A.

Van Den Akker, J.A. 1952. A note on the theory of fiber-fiber bonding in paper; the influence on paper strength of drying by sublimation. TAPPI 35(1):13-15.

Wilson, W.S. 1951. The Mechanism of Fiber Bonding. TAPPI 34(12):561-566.

Zhuang, J. and Biermann, C.J. 1995. Neutral to alkaline rosin soap sizing with metal ions and polyethylenimine as mordants. TAPPI 78(4):155-162.

Bursting strength of paper. 1991. TAPPI Test Methods. Volume I. T 403 om-85.

Tensile breaking properties of paper and paperboard (using constant rate of elongation). 1991 TAPPI Test Methods. Volume I. T 494 om-88.

Folding endurance of paper (MIT tester). 1991. TAPPI Test Methods. Volume I. T 511 om-88.

Internal tearing resistance of paper (Elmendorf-type method). 1991. TAPPI Test Methods. T 414 om-88.