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Wet Strength Improvement of Paper Via Crosslinking of Cellulose Using Polymeric Carboxylic Acids and Aldehydes
(Under the direction of Charles Q. Yang)

The wet-strength resins currently used in papermaking industry are under environmental scrutiny for emission of carcinogenic formaldehyde or adsorbable organic halides. In this research, polycarboxylic acids, dialdehydes, and the combination of polycarboxylic acid and dialdehydes with poly(vinyl alcohol) (PVA) were investigated as potential environmentally friendly alternatives. Kraft paper was treated by "pad-dry-cure" process and evaluated for its wet strength, dry strength, Z-direction tensile strength, stretch, breaking energy, folding endurance, swelling, and water sorption.

Two polycarboxylic acids, low molecular weight (MW) poly(maleic acid) (PMA) and high MW poly(methyl vinyl ether-maleic acid) (PMMA), demonstrated similar efficiency for improving wet strength. However, PMA caused paper embrittlement and seriously reduced folding endurance, while PMMA significantly improved dry strength and folding endurance. Scanning electron microscopic examination revealed that the fibers in PMA-treated paper were less swollen when soaked in water than those in PMMA-treated one. Dry performance of PMA-treated paper was greatly improved by combining PVA into the crosslinking system.

Dialdehydes combined with PVA were also investigated as wet-strength agents. Glyoxal alone provided excellent temporary wet strength without the need of catalyst and exposure to elevated temperature, while glutaraldehyde alone imparted durable wet strength at the expense of folding endurance, particularly at high level of wet strength. Combining PVA as co-crosslinker significantly improved wet strength, dry strength, folding endurance, and water sorption of paper crosslinked by glutaraldehyde. The

glutaraldehyde/PVA system shows high efficiency at low curing temperature around 110^{o}C and pH close to neutral.

The location of crosslinks was vital to the properties of treated paper. The different behavior of wet-strength resins originated from the different distribution of crosslinks in the intrafiber and interfiber areas. Low MW crosslinkers were able to penetrate into the fiber interior to form inter-lamellae and inter-fibrillar crosslinks, while high MW resins tended to stay on the fiber surface and crossing areas to produce interfiber crosslinks. PVA reacted with glutaraldehyde, and PVA/glutaraldehyde promoted the formation of interfiber crosslinks. Compared with intrafiber crosslinks, interfiber crosslinks provided not only higher efficiency for improving wet strength but also extra benefit for improving dry properties of paper.

INDEX WORDS: Paper, Cellulose, Wet-strength resins, Wet strength, Tensile strength, Folding endurance, Crosslinking, Poly(vinyl alcohol), Dialdehydes, Glutaraldehyde, Glyoxal, Carboxylic acid, Poly(maleic acid), Maleic acid copolymer, Esterification, Acetalization, Fiber bonding.

WET STRENGTH IMPROVEMENT OF PAPER VIA CROSSLINKING OF CELLULOSE USING POLYMERIC CARBOXYLIC ACIDS AND ALDEHYDES

by

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DEDICATION

To my dear wife and friend, Ying Chen,

for her unlimited love, understanding, and support;

To my loving sons, Grant and Albert,

for the wonderful enjoyment they bring to the world.

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CHAPTER 1

INTRODUCTION

WHY WET STRENGTH IS NEEDED

It is common sense that paper loses most of its strength and stiffness when it is exposed to high humidity or soaked in water. Paper is a layered mat with a pore structure consisting of a network of cellulosic fibers, which are bonded together by interfiber hydrogen bonds [1]. When subjected to high humidity, paper absorbs water and swells [2], hydrogen bonds are destroyed [3], and paper loses most of its original dry strength. Many paper products have excellent dry strength but retain little of the strength when wetted. Wet strength becomes the most important property of paper for structural applications and many specific end-uses which need exposure to weather or water, for example, paperboard, carrier board, paper container, linerboard, corrugated board, packaging paper, wall and poster paper, tea bags, map, currency paper, banknote paper, etc [4]. Apparently, the drawback of weak wet strength should be overcome before the potential of paper can be reached.

HOW TO STRENGTHEN WET PAPER

The increased military and commercial needs for paper products resistant to humidity and water has spurred the development of wet-strength paper [4]. It has been suggested that paper with a wet strength of more than 15% of its dry tensile strength should be considered as wet-strength paper [5]. The untreated paper generally loses more than 92% of its dry strength within seconds of being saturated with water. Some chemical-treated paper loses its wet strength slowly when soaked in water, and paper made in this way is said to have temporary wet strength. Other wet-strength paper is able to withstand a long length of soaking in water, and this sort of paper is called permanent

wet-strength paper [6]. Before World War II, the only practical way for making wet-strength paper was parchmentizing process, in which the paper was impregnated with animal glues or regenerated cellulose [7]. Then, heat treatment at elevated temperature 210-450^{o}C was found to improve wet properties of paper [8, 9], but the process was not widely accepted because of limited effectiveness and severe embrittlement of paper. Formaldehyde was known to crosslink cellulose at low pH and high temperature to impart a high degree of wet strength to paper [10, 11]. However, the process was also rejected commercially because of the development of brittlement in the paper and the offensive odor of formaldehyde. During the period of 1935 to 1941, the use of thermosetting aminoplast (UF and MF) came into commercial use [6]. Adding certain water-soluble synthetic polymers at moderate levels to paper and curing *in situ* gives significant improvement of wet properties. During 1942 to 1950, stimulated by the war need and the expanding use in later peacetime, a rapid growth in the use of wet strength resins and wet strengthened paper products occurred. In the 1960s, a neutral cure type of thermosetting resin was introduced to avoid the acidity required for the cure of UF and MF resins.

The making of wet-strength papers has now entered into an era of extensive use of synthetic resins such as urea formaldehyde (UF), melamine-formaldehyde (MF), polyamide-epichlorohydrin (PAE), and other polymers such as polyethyleneimine (PEI), glyoxalated- polyacrylamide (G-PAM), and dialdehyde starch (DAS) [12]. The first three resins, i.e., UF, MF, and PAE are regarded as permanent wet strength agents, which enable the treated paper to withstand soaking by water and retain wet strength for a long time. These three chemicals are the most commercially important and occupy more than

90% of market share. PEI was the first group of wet-strength resins pioneered by Germany in 1930s, but they are only of very limited use today because of the problem of repulping. The other two resins, G-PAM and DAS, are regarded as temporary wet-strength agents, which account for around 10% market portion [12]. All of the above resins can be added to the stock suspensions or applied to the paper surface at level of 0.5 to 3% based on the mass of pulp fiber. The wet tensile strength is improved from less than 10% to up to 40-50% of dry tensile strength.

PROBLEMS OF CURRENT WET-STRENGTH RESINS

Environment legislation has made the aforesaid wet-strength resins (UF, MF, PAE) the subject of scrutiny [12-14]. Most commercial UF and MF resins contain about 2-5% free formaldehyde in the resins when supplied [13], although much effort has been made to reduce the free formaldehyde [15]. Reduced formaldehyde content has a detrimental effect on shelf life and effectiveness of the wet-strength resins. Thus, the last decade witnessed a tremendous decline of the usage of UF and MF resins. PAE has also been condemned for emission of adsorbable organic halogen compounds (AOX) from paper mills and treated paper [13-16]. AOX has been incorporated into legislation in America and particularly Europe. Concern has been also paid to the paper products themselves, particularly the paper in contact with food stuff is subjected to specific regulation. Many papermaking companies have come under the increasing pressure from the consumer association not to use any formaldehyde- and chlorine-containing chemical additives. As the concerns about working conditions and ecological contamination increase, more and more stringent legislation will restrict the usage of above-mentioned resins.

Academia and industry have geared up to meet the challenge. Since wet-strength agents have become an integral part of the paper industry, great efforts have been made to meet the requirements of the legislation. Some progress has been achieved in optimization of the resin formulations to lessen their ecological impact. Nevertheless, this progress cannot help the aforementioned resins avoid the concerns of increased stringent legislation in the long run. Meanwhile, the development of new effective wet-strength resin without formaldehyde and organic chloride is still in its infancy. Most of the current efforts have suffered from some difficulties [13], such as insufficient resin effectiveness, detrimental affects on dry properties, incompatible curing conditions, or high cost.

OBJECTIVRE OF THE INVESTIGATION

The first purpose of our study was to develop a new wet-strength resin without the disadvantage of formaldehyde and halogens, yet with comparable efficiency and low cost and still in line with the current state of the art.

Another aspect of the research was mechanism studies: how do wet-strength resins function to alter the wet and dry properties of paper? Where the resins are located in paper and how they react with paper's components play a critical role in the development of wet and dry performance of paper. The mechanism studies will undoubtedly contribute to the development of wet-strength resins, which are able to improve the paper wet strength and dry toughness to meet higher requirement for structural materials.

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CHAPTER 2

LITERATURE REVIEW

FIBER CHEMISTRY

Layered Structure of Paper

Paper is a layered sheet of interlocking cellulosic fibers held together by hydrogen bonds [1]. It is formed continuously by a pulsed filtration process from an aqueous suspension of cellulosic fibers with possible addition of some polymeric retention aids and inorganic fillers. The cellulosic fibers are highly hydrophilic and are readily wetted and swollen by water. During the sheet forming process, as water is evaporated, the wet fibers are drawn close by the surface-tension force and ultimately held together by hydrogen bonds between the hydroxyl groups in the opposing fiber surfaces. The layered structure of paper is in the range of 30-300 μm, and an individual fiber is about a few mm long and 10-50 μm wide. A sheet of writing paper of 100 μm thickness would therefore be expected to be 5 to 10 fibers thick.

Papermaking Fibers

In papermaking industry, the term "fiber" refers to any cell which is present in the pulp and may be fiber basic cell types-vessels, fibers, tracheids, parenchyma cells or ray cells-each with its own structure peculiarities [2].

Both hardwoods and softwoods are used for making paper and they have very different fiber morphologies and thus very different papermaking properties [1, 3]. In softwoods, more than 90% of the volume is made up of tracheids, which have a length between 1 and 5 mm, and a length to width ratio of 100 to 1. The lumen is several times wider than the cell wall thickness. In hardwood, about 50% of the volume of the wood is

made up of tracheids, being in the order of 0.5 to 3 mm, with an average of around 1mm and a very narrow width of around 20μm.

The fibers of softwoods are longer and stronger than those of hardwoods, and they make up the bulk of papermaking fibers [1]. However, they tend to form macroscopic flocs of entangled fibers during the sheet formation and result in a sheet of relatively heterogeneous mass distribution. Therefore, blends of softwoods and hardwood fibers are generally used to give an appropriate compromise between strength and formation.

Chemical Components of Fibers [1, 3]

The chemical components of wood are illustrated in Figure 2.1.

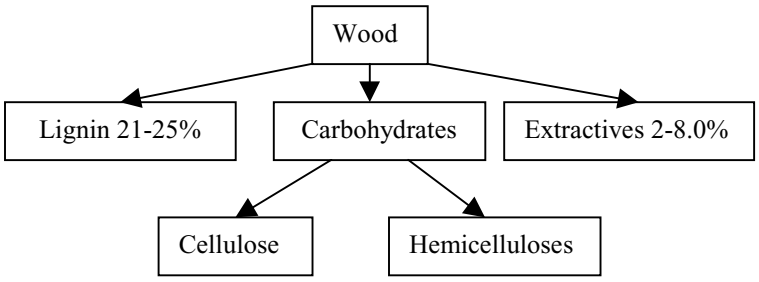

Figure 2.1 Chemical Components of Wood

Cellulose

Cellulose is the primary structural component of the cell wall with chemical formula $(C_6H_{10}O_5)_n$. The degree of polymerization (DP) varies with the different sources of cellulose and the treatments received (Table 2.1) [3]. Most pulp fibers have weight

average DP in the range of 600-1500. Cellulose in plant fibers is in several order of orientation in crystalline and amorphous regions.

Table 2.1 Degree of Polymerization of Cellulose (weighted averaged) [3]

Native Cellulose (in situ)	3500
Purified cotton linter	1000-3000
Commercial wood pulps	600-1500
Regenerated cellulose (e.g., rayon)	200-600

The bonding between papermaking fibers is conventionally considered to be primarily due to hydrogen bonds (H-bonds) (Figure 2.2). The bonding energy of an H-bond ranges from 8-32 kJ/mol, dependent upon the surrounding molecular structure because of inductive effects on the spatial charge distribution. The H-bonds between fibers hold together the fiber network of paper; the H-bonds between fibrils in the fiber wall give fibers their structural rigidity; and H-bonds between glucose units in the cellulose molecules participate in forming the cellulosic molecule. The three types of H-bonds have generally different strength.

Hemicelluloses

Hemicelluloses are non-structural heterogeneous polymers of hexoses (glucose, mannose, galactose) and pentoses (xylose, arabinose). They are usually branched and low molecular weight (DP~150-200). During chemical treatment of wood to produce pulp, the amount and structure of the various hemicelluloses usually change dramatically. The hemicelluloses are more easily degraded and dissolved than cellulose, so their percentage is always less in pulp than in original wood. It is widely

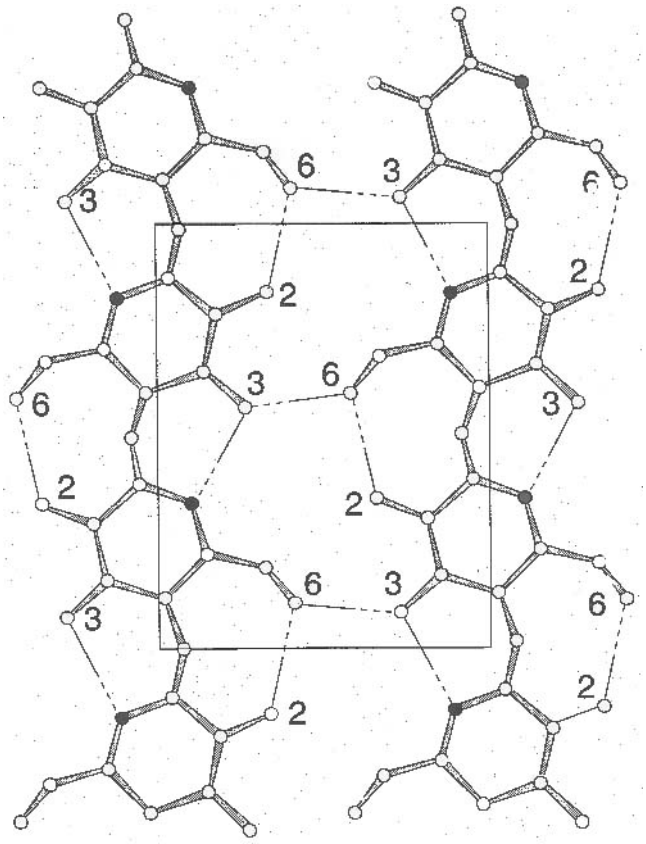

Figure 2.2. Hydrogen bonds between two cellulose molecules

recognized that they are beneficial to pulp and paper properties. The tensile strength of paper generally correlates positively with the hemicellulose content, because they become adsorbed to fiber surfaces to assist in fiber-fiber bonding.

Lignin

Lignin is an amorphous aromatic polymer of extremely complex structure. Its principal role is to form the middle lamella, an intercellular material which cements the fibers (tracheids) together in the wood. Lignin hardens the matrix (lignification) and provides additional support to the plant in addition to cellulose. Both lignin and matrix are present in greatest concentration in the middle lamellae and primary wall, and the

concentration decreases in the layers of secondary wall. The outer layer S_1 and inner layer S_3 are richer in lignin than middle layer S_2. Most of lignin is removed during pulping and beating. The residual lignin may cause paper to become brittle, and give rise to yellowing and discoloration as result of photochemical oxidation. The residual lignin can be removed by bleaching.

Resins and extractives

Resins and extractives are the components of small amounts (usually less than 5.0%) in wood. They are extractable by organic solvents such as ethanol or dichloromethane to produce the by-products of pulping such as turpentine and tall oil. The proportion of these extractives varies in hardwoods and softwoods and also between species.

Lamellation of Fiber Cell Wall [1, 2, 4]

A tracheid or "fiber" is a long and tapering cell which consisting of the vertical structure of softwood. The contiguous tracheid cells are separated and bound together by the middle lamella (M), an intercellular amorphous layer with very high lignin content. The wall of a typical tracheid or "fiber" consists of four distinct layers or groups of lamellae, as shown in Figure 2.3.

Primary Cell Wall

The primary cell wall (P) is a thin and relatively impermeable membrane ~0.05 μm around the cell, in which the fibrils form a loose reticulate network. Lignin and matrix (pectin and hemicellulose) are rich in this area.

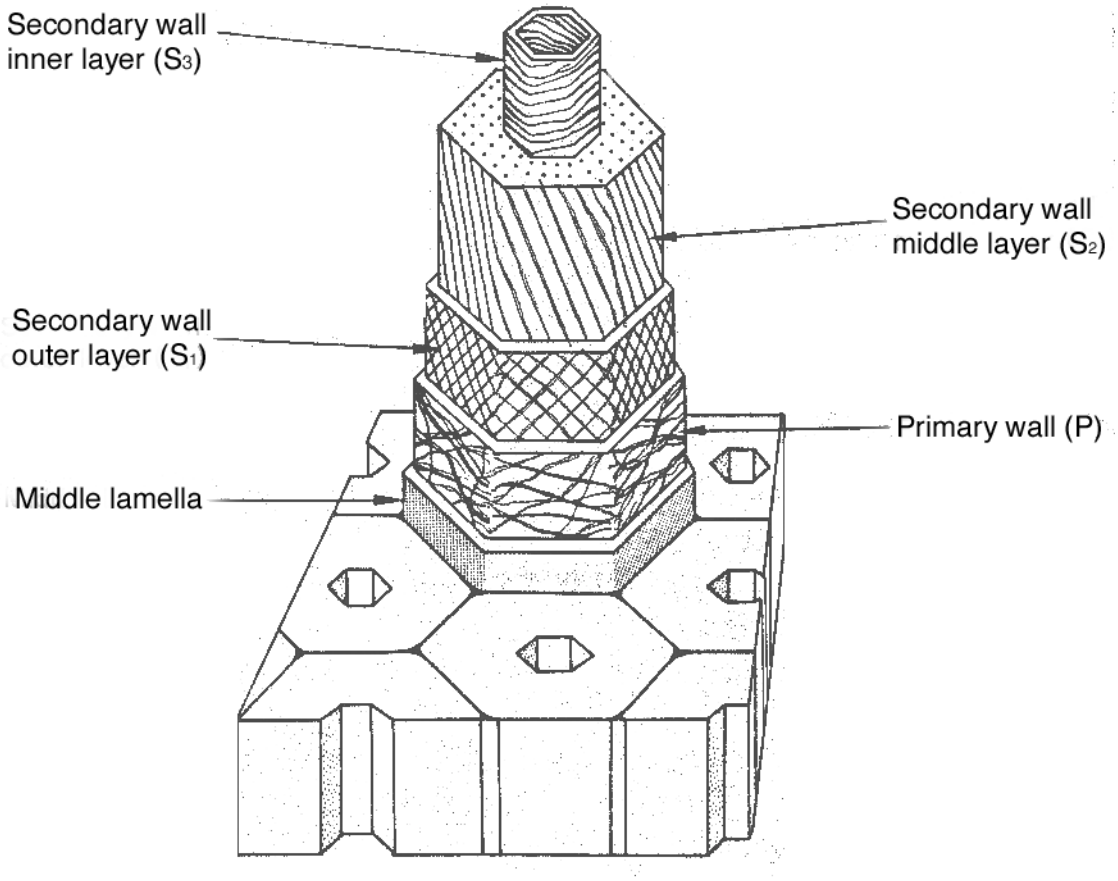

Figure 2.3 Diagrammatic representation of wall structure in a tracheid or fiber. The oblique lines on the faces of wall lamellae represent the run of the microfibrils [6]

Secondary Cell Wall

The secondary cell wall makes up bulk of cell wall and forms three distinct layers characterized by different fibril alignments. The outer layer S_1 with a thickness 0.1-0.2 μm consists of four to six lamellae, which spiral in opposite direction around the tracheid axis at an angle of 50-70^o. The middle layer S_2 with a thickness of 2-10 μm forms the main body of the fiber. The microfibrils in the S_2 layer spiral steeply around the cell axis at an angle of 0-30^o. The orientation of the microfibrils in the S_2 layer is important to the

mechanical properties of the fibers such as the modulus of elasticity. In general, the smaller is the spiral angle, the greater is the stiffness of the fiber and the greater is its resistance to creep in response to axial stress. The inner layer S_3 is thin (about 0.1 μm) and is not always present. Here the fibrils also follow a flat helix with a pitch of 60-90^o. The S_3 is sometime described as the tertiary wall mistakenly.

Tertiary Wall or Warty Layer

The tertiary wall or warty layer (T wall) is a very thin layer lining the cell lumen, which is the central canal of fibers (void).

Ultrastructure of Cell Wall [2, 4, 5, 6]

The plant cell lamellae consist of cellulose molecules arranged in numerous parallel fibrils, which are embedded in a continuous system of micro-capillaries filled with matrix substance. Figure 2.4 is the diagram of the ultra-structural composition of a cell wall layer.

The chains of cellulose combine to form an elementary fibril with an average width of 3.5 nm. The elementary fibril consists of well ordered regions of cellulosic chains, the crystalline areas, separated by rather disordered regions of the chains, the regions. Water can penetrate into the paracrystalline regions but not the crystalline ones.

The elementary fibrils are grouped together to form microfibrils of up to 25 nm diameter. The elementary fibrils of pure cellulose are embedded in a continuous

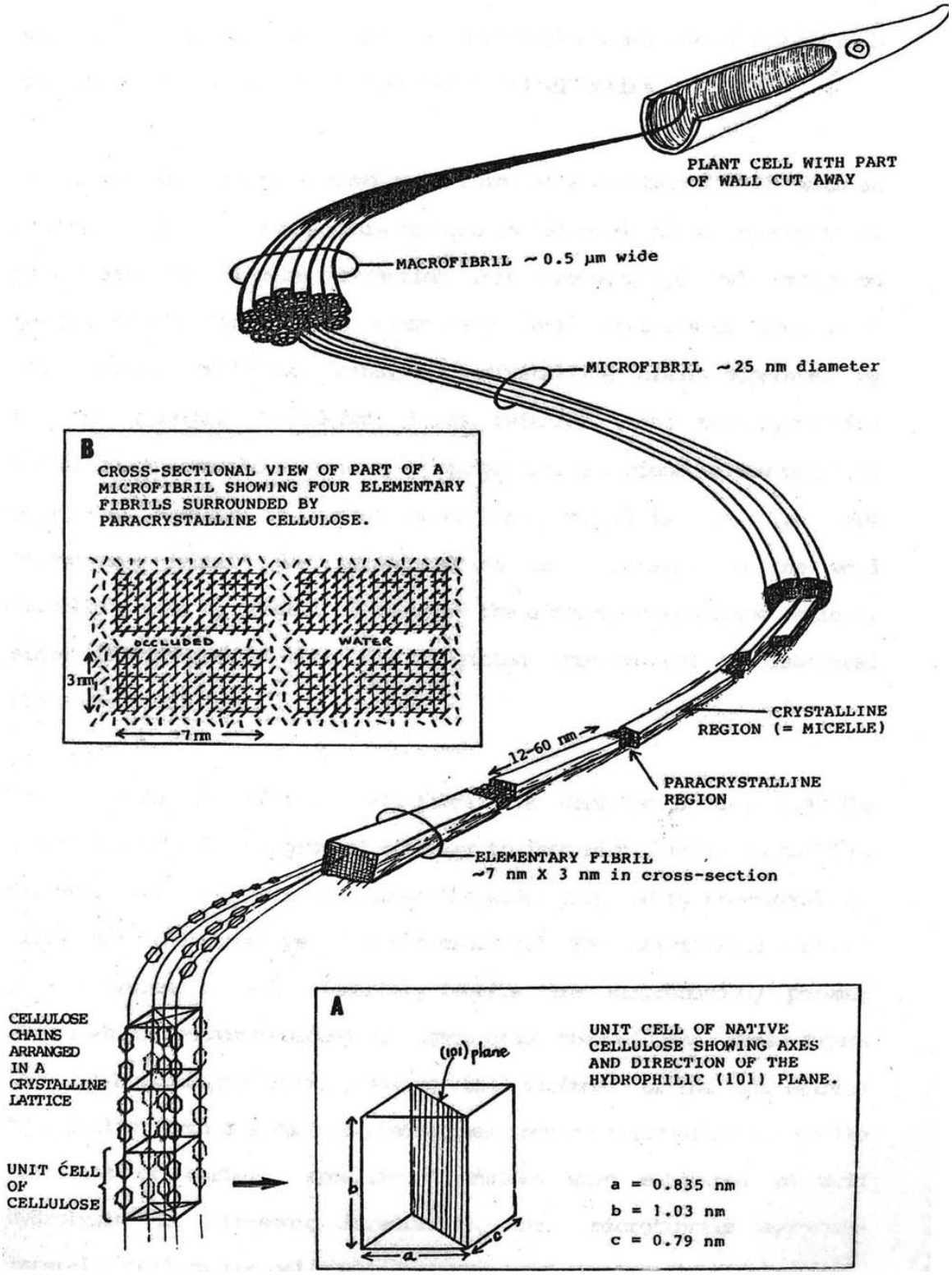

Figure 2.4 Diagram of the ultrastructural composition of a cell wall layer [2, 5, 6]

amorphous matrix consisting of pectin and hemicelluloses. The matrix is a hydrophilic gel with high swelling capacity and plastic deformability. It protects the cell from both mechanical damage and dehydration. The microfibrils aggregate laterally to form the cell wall lamellae, and the 101 plane (richest in hydroxyl groups) is considered to be the plane of lamellation. The microfibrils may be further aggregated into macrofibrils of up to 0.5 μm diameter.

Change of Fiber Cell Wall During Papermaking Process [2, 3, 5, 6, 7]

Cellulose fibers possess a number of properties required for papermaking (Table 2.2). In general, the best balance of performance occurs when most of lignin is removed but substantial amount of hemicellulose retained. The fiber strength depends upon the nature of raw material and the method of pulping, while the paper strength depends not only upon fiber strength but more upon the fiber-fiber bonding. Beating or refining tends to optimize the bonding at the expense of individual fiber strength.

Table 2.2. Properties of Cellulose Fibers [3]

- High tensile strength
- Suppleness (flexible, conformability)
- Resistance to plastic deformation
- Water insoluble
- Hydrophilic
- Wide range of dimensions
- Inherent bonding ability
- Ability to absorb modifying additives
- Chemically stable
- Relatively colorless (white).

Pulping

Pulping is a process to reduce the wood chips into separated fibers by removing the lignin from the middle lamellae. The integrity of the cell wall layers is retained. Pulping modifies fiber characteristics, changes chemical composition of cell wall components, and redistributes the hemicelluloses according to the pulping process and pulping degree. Extraction of the matrix from the fibers results in an extensive interfibrillar capillary system, and thus a great increasing swelling ability. The commercial pulping processes are classified as mechanical, chemical (alkaline Kraft process and acidic sulfite process), and semichemical (combination of mechanical and chemical processes) pulping.

Beating or Refining

Beating or Refining is the most important process for fibers to develop pulp suspension and sheet-forming ability. Refining is a continuous operation while beating is a batch operation, even though the two terms are used interchangeably frequently. In the refining process, fiber suspension is forced to circulate between a stationary metal plate (stator) and a moving metal plate (rotor). Both mechanical and hydraulic forces are involved in altering fiber characteristics, in terms of external fibrillation, internal fibrillation (or cell wall delamination), release of soluble carbohydrates, fiber shortening, generation of fines, fiber curling, et al.. Figures 2.5 and 2.6 show the effect of beating on the structure of chemical pulp fibers.

External fibrillation is the producing of "fuzz" or "pile" of very fine filaments on fiber surface. As beating proceeds, cell wall layers are split, and the fibrils unravel and become raised up on the fiber surface, so the surface area of fibers is greatly increased. The primary wall remaining on the fibers after pulping is removed, and the outer

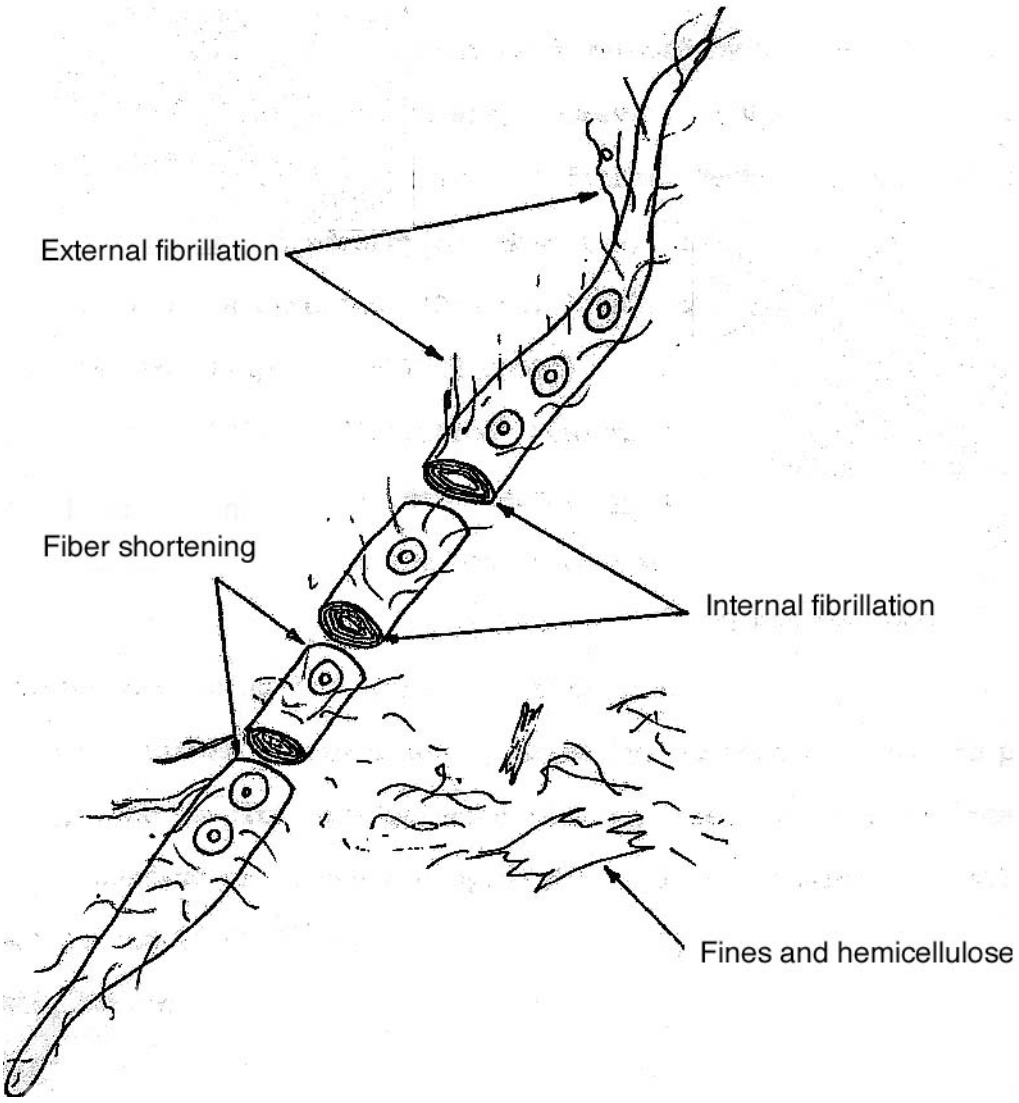

Figure 2.5 The effect of beating on a chemical pulp fiber [7]

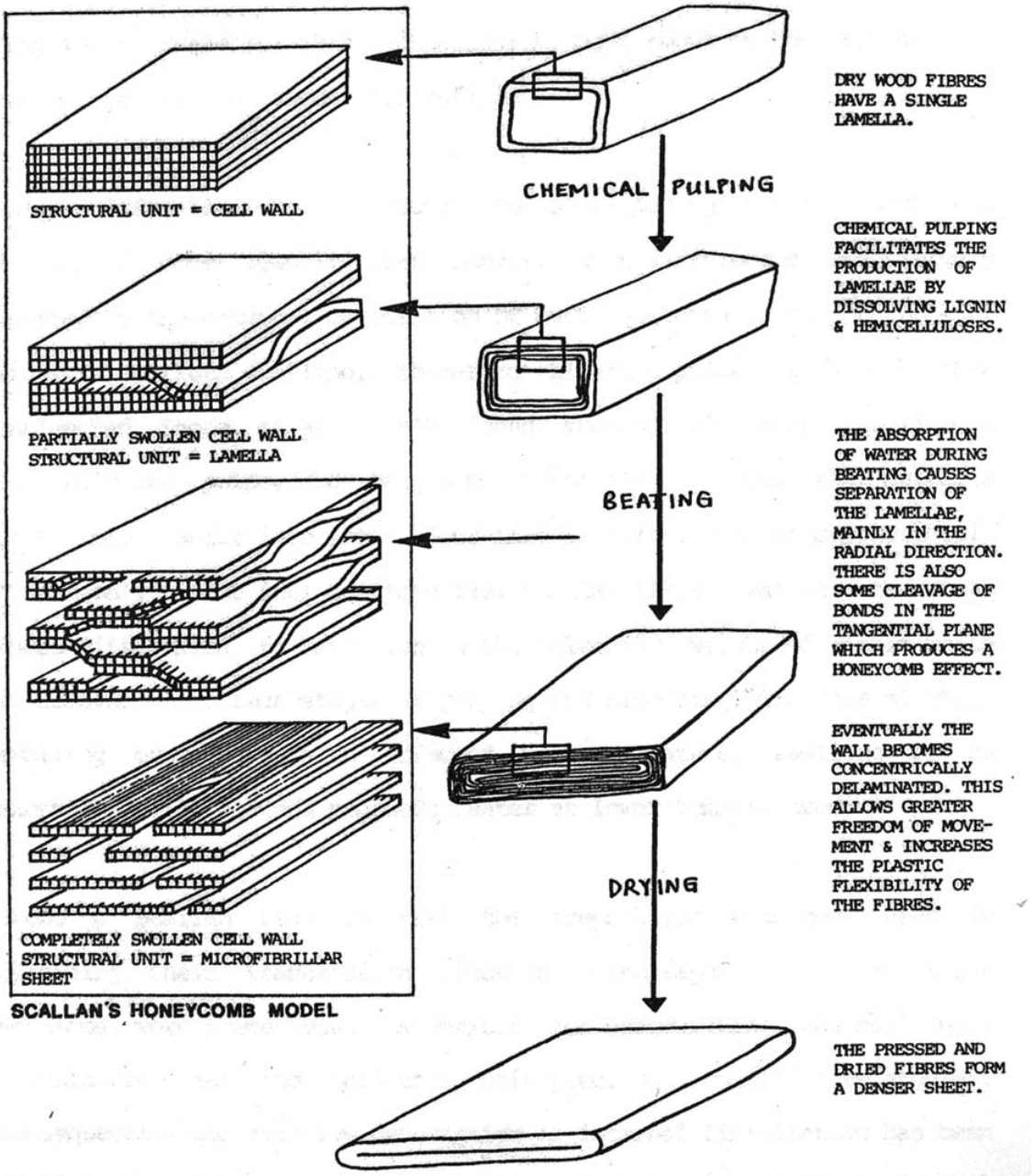

Figure 2.6 The development of internal fibrillation by chemical pulping and beating [2]

secondary wall is ruptured and partly removed to allow the middle secondary wall to swell freely.

Internal fibrillation, also called cell wall delamination, is the splitting apart of the cell wall layers into their constituent lamellae. The microfibrils making up the lamellae have greater adhesion in the tangential than in the radial direction. As beating proceeds, the fiber wall is delaminated into thinner and thinner coaxial layers. Cleavage also occurs in the tangential direction, thus creating an "honeycomb" structure with pores of a few nm, as shown in Figure 2.6. The "honeycomb" structure possesses effective local plasticity in the cell wall and conformability of fibers, which is essential for sheet formation. As the fibers become soft and flexible, the cell wall, on drying, tends to collapse into the lumen, giving a ribbon-like structure.

Bleaching

Bleaching removes residual lignin. Because lignin restricts the swelling of hemicelluloses, its removal from between the coaxial lamellae of the cell wall increases the swelling ability and flexibility of fibers.

WET STRENGTH OF PAPER

Paper is a layered mat of cellulosic fibers which are held together by interfiber hydrogen bonds. Due to their high hydrophilicity, cellulose fibers are readily wetted and swollen by water, and the moisture content of paper increases with environmental humidity [8]. Because hydrogen bonds are vulnerable to attack by water, the amount of fiber-fiber hydrogen bonds and thus the strength of paper decreases steadily as the moisture content of paper increases [9]. Precise testing of various papers without artificial

bonding shows a range of tensile strength retention from 1 to 8 percent on complete saturation with water [10]. It is thought that some of the residual strength comes from covalent fiber-fiber bonds produced during papermaking [11].

Since low wet strength results from the breaking of fiber-fiber bonds by water, the solution of the problem lies in the protection of pre-existing inter-fiber hydrogen bonds or the introduction of new bonds that will not be disrupted readily by water. Ionic and/or covalent bonds can be used to achieve this goal [12, 13]. Because the enthalpy of ionic bonds (5-20 kcal/mol) and, particularly, covalent bonds (~80 kcal/mol) is much higher than that of hydrogen bonds (<5 kcal/mol), they are more stable in water. Therefore, many approaches using covalent and/or ionic cross-linking have resulted in the improvement of wet properties of paper. In general, wet strength additives are water-soluble and chemically reactive polymers. These polymers can react themselves (homo-crosslinking) to create a restraining network or react with fiber components (hetero-crosslinking) to produce fiber-resin-fiber bonding on the paper surface. At present, two principal wet-strength mechanisms have been used for the explanation of development of wet-strength by resins [10, 14].

Protection

Protection has been widely accepted as the primary mechanism of wet-strength development by current wet-strength resins. Protection of pre-existing bonds may be accomplished from several ways. (1) The resin may cross-link itself to produce a 3-dimensional restraining network. (2) The additives can penetrate into the paper or move toward the fiber crossover areas to react with cellulose and form fiber-resin-fiber covalent cross-links. (3) The resins can form a protective skin of polymer by simple film

formation or by strongly irreversible adsorption. The covalent crosslinks and restraint network produced by the wet strength resins are insensitive to water attack and thus provide a shield for fiber-fiber hydrogen bonds. They restrict the access of water, prevent water from penetrating and swelling the cellulose web, help hydrogen bonds survive from water attack and function as they do in the absence of water, and thus preserve some fraction of the original dry strength.

Reinforcement

The network created by the wet strength resins supplements the web structure with additional load-bearing ability. This reinforcement mechanism can be deduced from the fact that most polymeric wet strength resins also increase the dry strength of paper to some extent. The increase of dry strength comes from the improved inter-fiber bonding brought about by covalent fiber-resin-fiber crosslinking [15]. The covalent bonds remain effective and provide strength to wet paper even after all inter-fiber hydrogen bonds are destroyed by water. The reinforcement factor has been considered only as a minor contributor to wet strength.

WET-STRENGTH RESINS AND THEIR USES

Small Molecular Cross-linkers

Formaldehyde

Formaldehyde has a strong tendency to cross-link cellulose fibers through the reaction with hydroxyl groups of cellulose at low pH and high temperature [16,17]. The process includes treating the paper or paperboard with formaldehyde solution or vapor in the presence of acidic catalysts (HCl, H_2SO_4, $ZnCl_2$, SO_2, etc.) then heating at high

temperature and dehydration conditions. Paper treated in this way develops a high degree of wet strength but suffers from severe brittleness. Caulfield and his colleagues [18-20] investigated the use of SO_2 and acid catalysts for crosslinking of cellulose with formaldehyde and improved the process for treatment of paperboard. The studies showed that non-restraining acetal bonds, which occur when one formaldehyde molecule attaches to one cellulose at two sites or two cellulose molecules in the same fiber lamella, do not contribute to dimensional stability and wet strength. Effective acetal bonds should cross-link between cellulose surfaces that would be separated by the swelling action of water without the restraint afforded by the crosslinking. The formaldehyde treatment process is no longer used commercially because of the concern about formaldehyde carcinogenicity.

Glyoxal

Glyoxal has been shown to produce weak crosslinks with cellulose by means of hemiacetal links. Paper treated with glyoxal develops wet strength immediately on drying and requires no after-cure or storage [21, 22]. Due to the susceptibility of hemiacetal to water, the wet strength is temporary and disappears after being soaked for several minutes. In textiles, glyoxal treatment catalyzed by Lewis acids has been investigated as a formaldehyde-free DP finish for cotton fabrics [23]. With acidic catalysts, glyoxal reacts with cellulose to form acetal bonds which are more stable in the presence of water. However, the treatment causes severe embrittlement of paper.

Urea-formaldehyde (UF) and Melamine-formaldehyde (MF) Resins

Formaldehyde-based thermosetting resins [24-27] UF and MF have been the classical wet-strength resins for papermaking. From 1935 to 1941, thermosetting aminoplast resins made debut on commercial market to meet the military need for durable packaging materials. The original application method was impregnation of paper sheets with low-molecular weight UF resins. Then the technique was developed to a stock treatment with anionic B stage UF resins and alum. Currently, nearly all commercial UF resins are cationic resins, which are made by modification with ethylenediamine, diethylenetriamine and other water-soluble multifunctional amines. Cationic UF and MF resins are readily absorbed by pulp fibers and useful for stock treatment without the aid of alum. UF and MF resins are generally considered to self-crosslink to form a 3-dimensional restraining network. However, MF resins show some signs of hetero-crosslink with cellulose by a "reinforcement" mechanism. Photographs show that tensile failure of MF strengthened paper occurs in the fiber wall rather than at fiber-fiber contact. Both UF and MF require acidic papermaking conditions for best performance.

UF resins are cheap, readily repulpable, and less susceptible to interference by other substances in papermaking system. They are widely used in making paper towels, tissue paper, paper plates, bag paper, and wet-strengthened linerboard. MF resins are more expensive than UF resins, but they provide permanent, high wet and dry strength to paper, and a significant increase in folding endurance. MF resins find specific applications, such as currency paper, map paper, photographic paper, and other papers which need permanent wet strength.

Polymeric Amine-Epichlorohydrin Resins [28-32]

The neutral and alkaline papermaking process stimulated the development of polymeric amine-epichlorohydrin resins in 1950s. The resins are prepared by reaction of polyamine or amine-containing polymers with epichlorohydrin in aqueous solution. Based on the polymers used, the resins can be classed as polyamide-epichlorohydrin (PAE), polyalkylenepolyamine-epichlorohydrin (PAPAE), and amino polymer-epichlorohydrin (APE). The backbone polymers offer primary, secondary, or tertiary amine groups to react with epichlorohydrin, and thus produce resins with different functionality, i.e., azetidinium and epoxide. With highly cationic charges, the resins are substantive to negatively charged pulp fibers and are readily adsorbed when added to papermaking systems. The resulting wet-strength is permanent and paper products cannot be easily repulped under acidic and slightly alkaline conditions. Since their inception in 1950s, the resins have found application in virtually every grade of paper products, and they account for 90% of the market share of wet-strength resins in North America. The detailed mechanisms are still unknown. Most researchers accept the self-crosslinking of the resins as the primary mechanism. Some researchers [14] suggested that azetidinium of the resins can react with carboxylate groups of hemicellulose, even though not with hydroxyl groups of cellulose.

Glyoxalated Polyacrylamide (G-PAM) Resin [33]

Since the emergence in late 1960's, glyoxalated polyacrylamide (G-PAM) resins have developed to be important wet-strength resins just second to polymeric amine epichlorohydrin resins. The resin is prepared by crosslinking low molecular weight

polyacrylamide (PAM) with sufficient glyoxal to react with most, but not all, of the PAM backbone amide groups. The crosslinking is controlled to the desired degree so that a certain amount of reactive aldehyde groups are left on the resin. The wet-strength development involves the formation of covalent hemiacetals between reactive aldehyde and cellulose among fibers and within fibers. The reaction of G-PAM resin with cellulose is rapid at neutral pH and even more at acidic pH (4-6) conditions, reaching most of its wet-strength potential in paper machine. Since the formation of hemiacetals is reversible in the presence of water, the wet-strength of the treated paper gradually decreases after soaking in water. In addition to wet strength improvement, G-PAM resins significantly improve the dry strength, flexibility, and adsorbence of treated paper. Therefore, G-PAM resins are principally used in tissues and paper towel.

Poly(carboxylic acid)s [34-44]

Multifunctional carboxylic acids have been extensively investigated as environmentally friendly DP finish for cotton fabrics to improve wrinkle resistance [34, 35]. The polycarboxylic acids include butanetetracarboxylic acid (BTCA) and citric acid. These acids have also been investigated as cellulose crosslinking agents for modifying the wet performance of paper [36-43]. The earliest report about this approach for wet-strength was given by Neogi and Jensen [36]. Then Horie and Biermann [39] treated bleached kraft handsheet with a BTCA aqueous solution and cured at 160^{o}C for 5 minutes. D. F. Caulfield [40] investigated the wet and dry properties of paperboard treated with BTCA and citric acid at concentrations of 4-10% and cured at 180^{o}C for 1.5 minutes. Y. J. Zhou [37, 38] also investigated the crosslinking mechanism of paper with

multifunctional carboxylic acids. These researches concluded that polycarboxylic acids crosslinking greatly improves the wet strength and wet stiffness of treated papers but notoriously sacrifices the toughness of paper, i.e., causing a dramatic reduction of folding endurance, stretch, and tensile energy absorption. Among various polycarboxylic acids investigated, BTCA is the most effective crosslinking agents for both cotton and paper. However, the extremely high cost of BTCA has prevented its use in commercial application. Xu, et al [41-43] have found that poly (maleic acid) (PMA) is as effective as BTCA in improving the wet-strength of paper but is much more cost-effective than BTCA. However, PMA also suffers from a similar drawback in causing brittleness in treated papers.

Xu and his colleagues [44, 45] used a high molecular weight maleic anhydride copolymers, poly(ethene-co-maleic anhydride) (PEMA), to improve the wet performance of paper. It was found that the high molecular weight polycarboxylic acids not only exhibited higher efficiency for improving wet strength but also significantly improved the dry strength and folding endurance of the treated paper. Based on the same esterification degree, paper treated with PEMA exhibits higher wet strength. It was believed that the high molecular weight (MW) crosslinking agents prefer formation of interfiber crosslinks, while small MW ones produce predominantly intrafiber crosslinks. Intrafiber crosslinking causes stress concentration and increases brittleness of the paper network, while interfiber crosslinking improves dry strength without hurting flexibility of paper.

Even though the PEMA is able to improve the wet and dry performance of paper simultaneously, they still suffer from two drawbacks. One is the high curing temperature (about 170^{o}C) required for effective crosslinking. Such a high temperature is not

compatible with current paper machine conditions (~130^{o}C). The second shortcoming is the low pH, about 2.8 necessary for effective reaction.

Comparison of Commercial Wet-strength Resins

The properties of currently used wet-strength resins are compared in Table 2.3.

Table 2.3 Comparison of currently used wet-strength resins [46]

Resin	MF	UF	Glyoxal/PAM	PAE
Principal advantages	Permanence Low cost	Low cost Easier repulping	Neutral sheet Dry strength Repulping Temporary	Neutral /Alkaline Retention Permanence
On-machine cure(%)	50-60	20	60-95	10-30
Time to 100% cure (weeks)	1-2	1-4	1-2	1-2
pH range	4.0-5.5	3.8-4.5	4.5-7.5	5.0-9.0
Preferred pH	4.5	4.0	6.0-7.0	8.0
Solid content(%)	12% (regular) 10% (HE)	25-40	6-10	12-33
Addition point	Usually thick stock	Thick stock	Thick or dilute	Thick or dilute
First pass retention(%)	60	35	40	80
Major precaution	Sulphate level	Low pH	Sulphites pH over 7.5	Chlorine chemicals
Broke handling	High temperature Low pH	Easier than MF	Easiest Helped by high temperature	Hypochlorite or high pH and temperature
Absorbency	Poor	Fair	Best	Good
Sheet brightness	Fair	Good	Best	Fair
Usual drainage	Slower	No effect	Slightly faster	Faster
Storage (24^{o}C) (weeks)	1	12-24 at low solids	1 (10%) 4(7.5%)	12
Relative cost	53	29	100	100
Affect on sizing	Much improved	Little	Improved	Much improved

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CHAPTER 3

COMPARISON OF THE KRAFT PAPER CROSSLINKED BY POLYMERIC CARBOXYLIC ACIDS OF LARGE AND SMALL MOLECULAR SIZES: DRY AND WET PERFORMANCE[1]

[1]Xu, G. G. and C. Q. Yang. 1999. Journal of Applied Polymer Science 74: 907-912. Reprinted here with permission of publisher

ABSTRACT

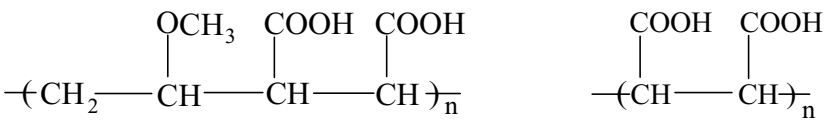
Polycarboxylic acids have been used as crosslinking agents for wood pulp cellulose for improving paper wet strength. Our previous research showed that low molecular weight polymeric carboxylic acids are effective in improving paper wet strength retention while reducing its flexibility. In this research, we compared two polymeric carboxylic acids, i.e., poly(maleic acid) (PMA) with an Mn of 800 and poly(methyl vinyl ether-co-maleic acid) (PMMA) with an Mn of 1,130,000, for improving paper wet strength. The Kraft paper sheets were treated at 2.0% acid level and cured at different temperatures. The dry strength, wet strength and folding endurance of the treated sheets were measured. We found that PMA and PMMA have comparable effectiveness in improving paper wet strength and wet stiffness. However, the treatment with PMA increases paper brittleness and severely diminishes paper folding endurance, whereas the treatment with PMMA increases both the dry strength and folding endurance by enhancing the paper's toughness. This striking difference in the performance of the treated paper is attributed to the different nature of the crosslinkages formed on the sheets.

***Key Words**: carboxylic acids, cellulose, crosslinking, esterification, paper, polymeric acids, strength, wet strength resins, folding endurance, wood pulp.*

INTRODUCTION

Polycarboxylic acids were originally developed as nonformaldehyde crosslinking agents for cotton (1). Previous studies have shown that multifunctional carboxylic acids have the potential to become environmentally friendly wet strength agents of paper. Horie and Biermann reported that the bleached Kraft handsheets treated with 1,2,3,4-butanetetracarboxylic acids (BTCA) show significantly improved wet strength (2). Caulfield studied the dry and wet performance of unbleached Kraft board treated with BTCA and citric acid (3). Zhou and Luner investigated the treatment of paper with BTCA, tricarballylic acid and succinic acid, and found that BTCA is the most effective crosslinking agent for wood pulp cellulose (4, 5). To overcome the high cost of BTCA, we applied cost-effective poly(maleic acid) (PMA) as a wet strength agent, and found that PMA is equally efficient as BTCA for improving wet performance of paper (6-8). We also found that linear relationships exist between the amount of ester formed on the paper and wet strength retention, dimensional stability, wet stiffness of the treated paper, indicating that the improvement of wet performance of the treated paper is directly attributed to the ester crosslinking of cellulose (7). The treatment using BTCA, PMA, and other polycarboxylic acids with relatively small molecular sizes causes severe fiber embrittlement, and consequently reduces the folding endurance of paper (7, 8).

In this research, we compare the effects of two polymeric carboxylic acids, i.e., PMA with a number average molecular weight (Mn) of 800 and poly(methyl vinyl ether-co-maleic acid) (PMMA) with an Mn of 1,130,000 (Scheme 1), on dry/wet strength and other mechanical properties of the treated paper.



PMMA (Mn=1,130,000) PMA (Mn=800)

Scheme 1 Chemical structures for the polymeric carboxylic acids

EXPERIMENTAL

Materials

The unbleached Kraft paper used in this research was a commercial product with 65g/m^2 manufactured by Southwest Paper, Georgia. PMA with an Mn of 800 was a 50% aqueous solution made by FMC. Sodium hypophosphite (NaH_2PO_2) and PMMA with Mn of 1,130,000 were supplied from Aldrich. The solutions used to treat the paper sheets consisted of 2.0% PMA or PMMA in combination with 1.0% sodium hypophosphite as a catalyst.

Paper Treatment

The Kraft paper sheets with a size of 25x25 cm^2 were immersed in a solution for 30 seconds, then pressed between squeezing rolls to remove excess liquid to reach about 95% wet pick-up. The impregnated sheets were dried on a hot plate dryer at 85 ^{o}C for 3 min to prevent curling. Each sheet was cured in a forced draft oven at specified temperatures ranging from 140 to 180 ^{o}C for 1.5 min. The cured sheets were rinsed in running water for 15 minutes to remove unreacted chemicals, and then dried. Five specimens were treated under each condition.

Paper Performance Testing

Dry tensile properties, wet tensile properties and folding endurance of the paper sheets were evaluated according to TAPPI standard test methods T 494 om-88, T456 om-87, and T 511 om-96, respectively. The tensile properties measured included tensile strength, stretch, tensile energy absorption, energy absorption to 0.2% yield point, and Young's modulus. For wet tensile testing, the specimens were first immersed in distilled water for 24 hours. Ten measurements were performed for each testing procedure.

RESULTS AND DISCUSSION

The Wet Properties of the Treated Paper

The Kraft paper treated with 2.0% PMA and 2.0% PMMA in the presence of 1.0%NaH_2PO_2 as a catalyst was cured at temperatures ranging from 140 to 180^oC for 1.5 min. The wet/dry strength ratios of the paper sheets cured at different temperatures are presented in Figure 3.1. Because PMMA increases dry strength while PMA has little effect on the dry strength of treated paper, we use the ratio of the wet strength of treated paper to the dry strength of the control sample (W/D) as the basis to compare the wet strength of treated paper. The data show that the wet strength increases as the curing temperature increases. It is evident that the wet strengths of the PMA-treated and PMMA-treated sheets demonstrate similar temperature dependence and that the effectiveness of PMA and PMMA for improving wet strength of paper is comparable. The increase in wet Young's modulus of the treated paper sheets is shown as a function of curing temperatures in Figure 3.2. The similarity between the PMA and PMMA

treatments as illustrated in Figure 3.2 indicates that PMA and PMMA are equally effective in improving the paper wet stiffness.

The wet strength retention of paper is determined to a large extent by the fiber-fiber bonds in paper (10). The diminished tensile strength and stiffness of paper under wet conditions is a result of water penetration into the paper, the swelling of the cellulose fiber, and consequently the destruction of the hydrogen bonds which hold the fibers together. It is believed that the amount of surviving hydrogen bonds is the overriding factor in retaining wet strength of paper (11). Therefore, the effectiveness of a crosslinking agent depends on its ability to create a crosslinking network to restrain the cellulose structure and to protect the existing hydrogen bonds from the disruption of water. For a crosslinking agent of high molecular weight, such as PMMA, the large molecular size prohibits it from passing through the fiber wall into the interior (12). Therefore, the predominant bonds formed by PMMA on paper are inter-fiber crosslinks.

Our previous studies showed that the improvement of wet strength of the paper treated with low molecular weight crosslinking agents such as BTCA and PMA is directly attributed to ester crosslinking of wood cellulose (7). A crosslinking agent of small molecular size is able to penetrate easily through pores on the cell wall into the bulk of wood cellulose fibers. Therefore, the predominant bonds formed by PMA are intra-fiber crosslinks between cellulose molecules. The intra-fiber crosslinks formed by a small

crosslinking agents prevent the swelling of the fibers, preserve the hydrogen bonds among the fibers, and improve the wet strength of the treated paper.

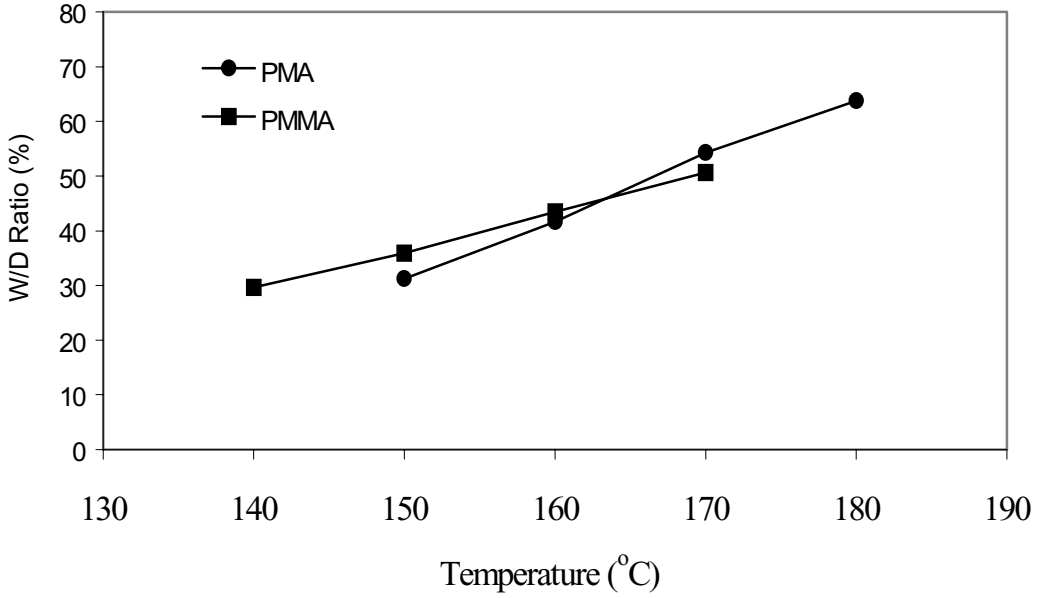


Figure 3.1 Wet strength (W/D ratio) of the Kraft paper treated with 2.0% PMA and 2.0% PMMA, and cured at different temperatures

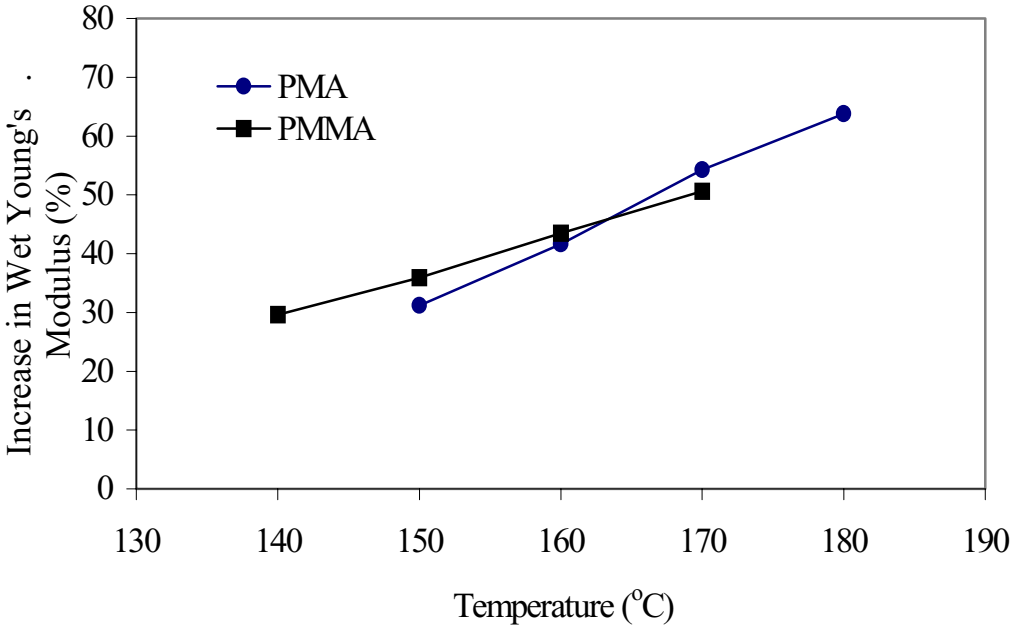


Figure 3.2 Increase in wet Young's modulus of the Kraft paper treated with 2.0% PMA and 2.0% PMMA, and cured at different temperatures.

In this research, the paper sheets were treated with PMA and PMMA of equal concentration (2.0%, w/w). However, the mole concentration of carboxylic acid groups for PMA is approximately 50% higher than that for PMMA because the methyl vinyl ether repeating unit in PMMA is inactive for crosslinking cellulose. Secondly, the carboxylic acid groups of PMMA have less mobility to access cellulose hydroxyl groups of cellulose for esterification. Therefore, PMMA produces far less ester linkages with cellulose than PMA even if the PMMA and PMA solutions used to treat the paper have equal carboxylic acid mole concentrations. The data presented above indicate that PMMA and PMA with the same weight concentrations are equally effective in enhancing the wet strength and wet stiffness. Obviously, the crosslinks formed by PMMA have higher effectiveness than those by PMA in enhancing wet strength of paper. We believe that different mechanisms exist for the improvement of wet performance of paper by crosslinking agents of different molecular sizes.

The wet strength agents must locate at weak links of the fiber network that are vulnerable to the attack by water if they are to be effective. The individual fiber has a diameter in the range of 10 to 50μm, macrofibrils have a width around 0.5μm, and microfibrils have a diameter about 25 nm (13). The distribution of pore sizes on the fiber wall depends on the particular choice of wood species and control of the pulping process. For unbleached Kraft, the pore sizes distribute with a modal radius of about 1μm depending on the beating degree (14). PMA with an Mn of 800 has a mean extended molecular length round 1.7 nm. With a dimension much smaller than pore sizes, PMA molecules are able to enter the fiber interior freely. In contrast, the high molecular weight polymers, such as PMMA with an Mn of 1,130,000, cannot penetrate fiber walls (15).

However, driven by capillary and surface tension forces during drying process, they move towards the fiber cross-over areas where they produce inter-fiber crosslinks. Due to the same reason, polyacrylamide resins with a molecular weight between 100,000 and 500,000 are very effective in strengthening fiber-to-fiber bonding and widely used as dry strength additives to paper. Apparently, the long molecule chains of PMMA tend to form inter-fiber bonds, whereas the PMA molecules may only attach to the same fiber lamella, and form intra-fiber bonds. Therefore, even though fewer ester links are formed between PMMA and cellulose, the treated paper is still able to achieve the same level of wet strength and wet stiffness as that treated with PMA. When the curing temperature is below 160 ^{o}C, PMMA appears to be slightly more efficient than PMA (Figures 3.1 and 3.2).

The Dry Properties of the Treated Paper

Presented in Figure 3.3 is the change in dry tensile strength of the treated paper. A striking difference between PMMA and PMA is found in the impact on the dry strength of the treated paper. The PMMA-treated paper shows approximate 20% increase in dry tensile strength over the control sample, whereas the PMA-treated paper has little change in its dry strength after treatment. This significant difference is attributed to the different nature of the crosslinking formed by low and high molecular weight crosslinking agents.

The tensile strength of paper is determined by the intrinsic fiber strength as well as the amount and strength of fiber-to-fiber bonds (13). Crosslinking agents of small sizes can penetrate into the pore structure of cellulose cell wall and form intrafiber crosslinks. This is the reason why small multifunctional hydroxyl-reactive compounds have been

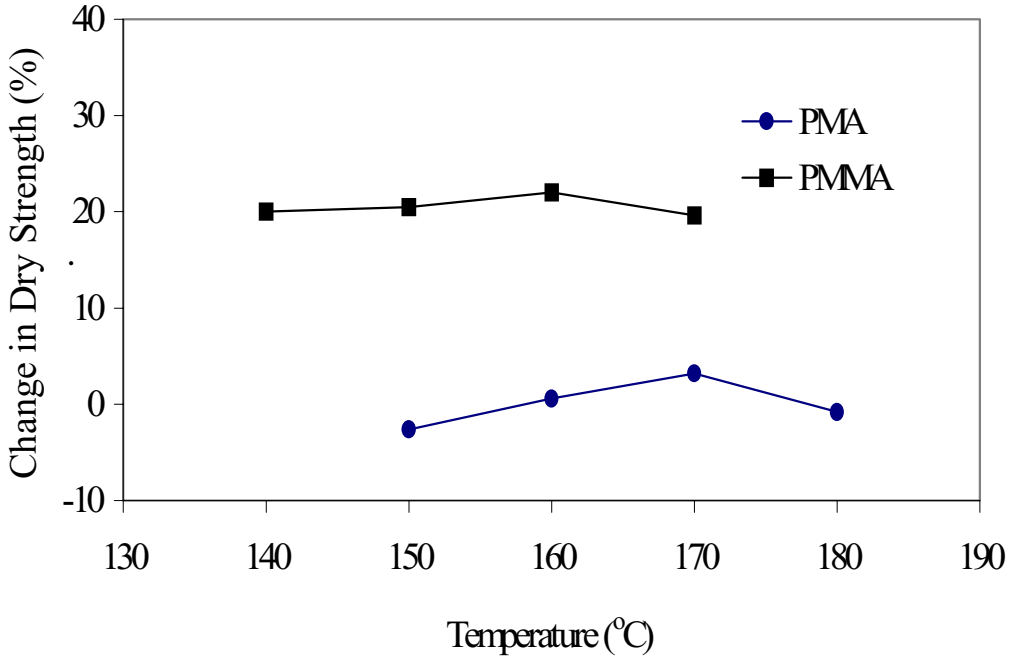


Figure 3.3 Change in dry strength of the Kraft paper treated with 2.0% PMA and 2.0% PMMA, cured at different temperatures.

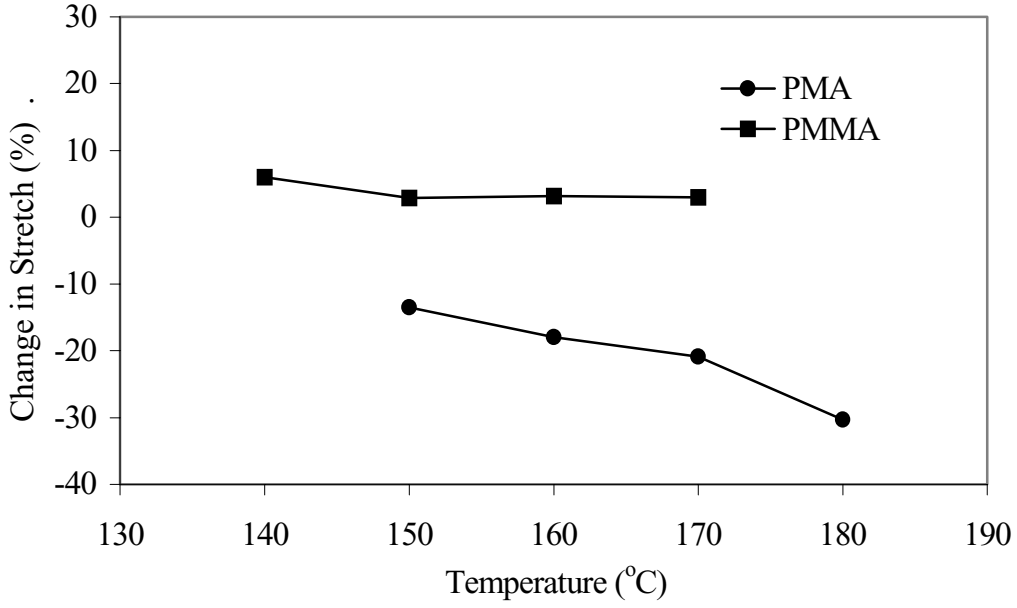


Figure 3.4 Change in stretch of the Kraft paper treated with 2.0% PMA and 2.0% PMMA, cured at different temperatures.

used to crosslink individual pulp fibers for producing high bulking resilient fibers (16,17). The intra-fiber crosslinks formed by these small molecular compounds have little effect on the dry tensile strength of the treated paper. The small size crosslinking agents, such as BTCA and PMA, form few interfiber crosslinks and thus essentially have no effects on the dry strength of the treated paper. Xu and his coworkers found that the Kraft paper treated with BTCA at different concentrations showed little change in its dry strength (8). For large size crosslinking agents, such as PMMA, the inter-fiber crosslinks reinforce the fiber-to-fiber bonds and thus result in a significant increase in the dry strength of the treated paper as shown in Figure 3.3.

Xu and his coworkers also studied the z-direction tensile strength of paper treated by poly(ethene-maleic acid) (PEMA) (Mn=100,000) and BTCA, and found that the Z-direction tensile strength of paper treated with PEMA was significantly higher than that treated with BTCA at the same levels of crosslinking (9). This finding provides a direct evidence that high molecular weight polymeric carboxylic acids favor the formation of inter-fiber crosslinks, thus reinforcing fiber-fiber bonding on the treated paper.

The extensibility and toughness of treated paper, expressed as stretch and tensile energy absorption (TEA), respectively, are shown in Figures 3.4 and 3.5. The PMMA-treated paper increases its stretch by 3-5%, whereas the PMA-treated paper decreases it by 15-30% (Figure 3.4). The PMMA-treated paper increases its tensile energy absorption by 22%, whereas the PMA-treated paper decreases by 13-30% (Figure 3.5). Apparently, PMMA treatment improves the toughness of the dry paper, whereas PMA treatment causes embrittlement and diminishes the toughness of paper.

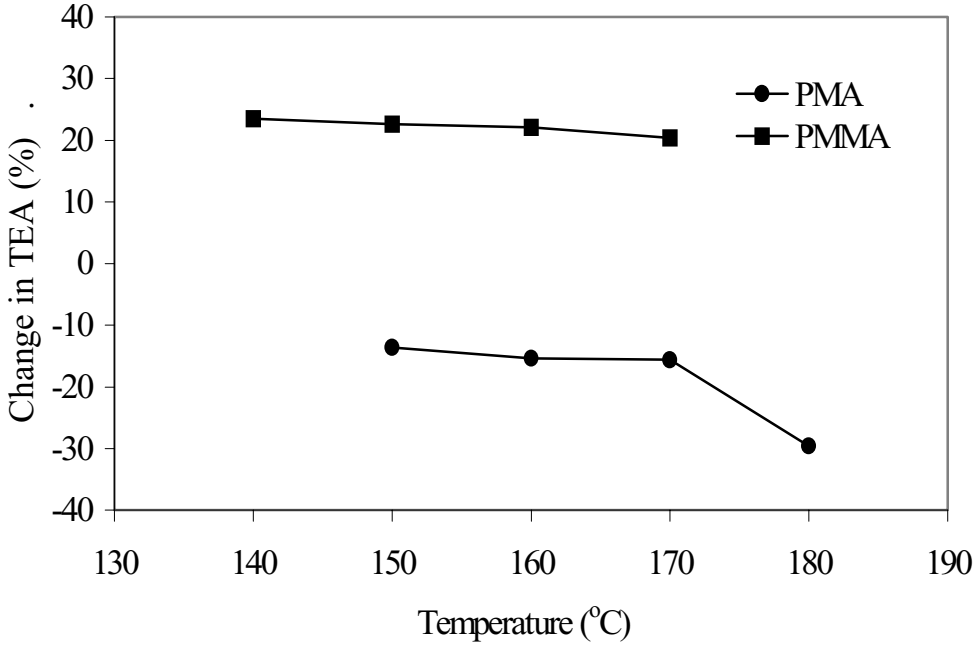


Figure 3.5 Change in tensile energy absorption of the Kraft paper treated with 2.0% PMA and 2.0% PMMA, at different temperatures.

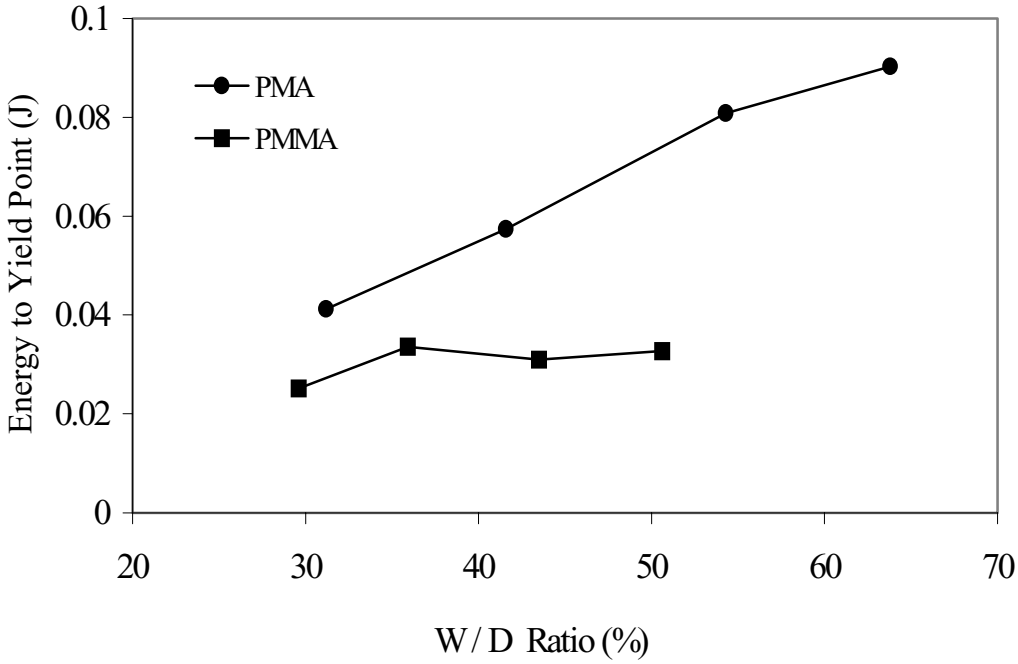


Figure 3.6 Energy to 0.2% yield point as a function of wet strength retention, paper treated with 2.0% PMA and 2.0% PMMA, cured at different temperatures.

The paper extensibility depends on not only the extensibility potential of the individual fibers, but also on the nature of the fiber network (18). The paper stretch increases as its tensile strength increases, because higher tensile strength reduces the possibility of premature fracture. The intra-fiber crosslinks induced by PMA limit the relative movement between adjacent cellulosic chains, thus reducing the extensibility of the fibers. The inter-fiber crosslinks formed by PMMA increase the tensile strength of the paper and thus improve the extensibility of the treated paper.

PMMA treatment significantly improves TEA, whereas PMA treatment reduces TEA as shown in Figure 3.5. TEA is the area under the stress-strain curve as the paper is stretched to rupture. TEA increases with increasing tensile strength, increasing stretch, or both. Stretch and TEA are two important factors for paper products that are frequently folded or exposed to stress during use. Low stretch causes localized built-up of high stress and rupture takes place under small load. Paper with high extensibility and high TEA can absorb stress and withstand heavy impact without breaking.

The energy to 0.2% yield point for the paper treated with PMMA and PMA is plotted as a function of W/D ratio in Figure 3.6. One observes that the energy to 0.2% yield point is much lower for paper sheets treated by PMMA than for those treated by PMA at the same wet strength level. It indicates that PMMA-treated paper demonstrates better sensitivity to stress and thus faster stress relaxation. Rapid stress relaxation facilitates distribution of stress on the paper to a much wider area, thus increasing tensile strength tensile energy absorption.

Folding endurance is another important parameter for wet strengthened paper. In our previous research, we found that paper treated by crosslinking agents of small size shows drastically reduced folding endurance (7). The folding endurance of the paper treated with 2% PMMA and 2% PMA is presented as a function of the W/D ratio in Figure 3.7. Folding endurance of the PMA-treated paper is lower than the untreated; meanwhile, it also decreases with increasing wet strength. For the PMA-treated paper, the benefit of higher wet strength achieved by higher curing temperatures is offset by the loss of flexibility and reduction in folding endurance. For the PMMA-treated paper, the folding endurance is better than that of the control, and it remains at a high level as wet strength increases. The change of folding endurance is consistent with the TEA and energy to yield point data presented in Figures 3.5 and 3.6, respectively.

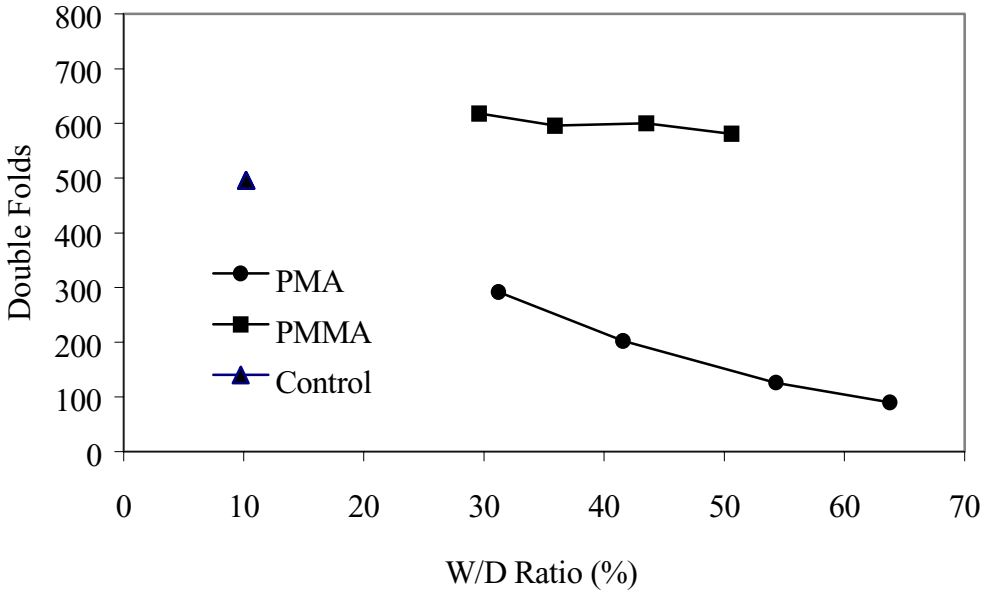


Figure 3.7 Folding endurance as a function of wet strength, Kraft paper treated with 2.0% PMA and 2.0% PMMA, cured at different temperatures

CONCLUSION

High molecular weight PMMA and low molecular weight PMA demonstrate comparable effectiveness in improving wet strength and wet stiffness of paper. PMMA treatment provides significant improvement in dry strength, tensile energy absorption and folding endurance of the treated paper, and it also increases stretch to a less degree. In contrast, PMA treatment causes severe reduction in stretch, tensile energy absorption and folding endurance. Paper treated with PMMA shows lower energy to yield point than that with PMA. The difference in the properties of the paper treated with these two polymeric carboxylic acids is attributed to the difference in their molecular sizes. High molecular weight PMMA favors formation of inter-fiber crosslinks, and thus improves dry strength and toughness. Low molecular weight PMA produces predominately intra-fiber crosslinks. This causes embrittlement of fibers, and diminishes the flexibility of the treated paper.

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CHAPTER 4

EFFECT OF POLY(VINYL ALCOHOL) ON THE STRENGTH OF KRAFT PAPER CROSSLINKED BY A POLYCARBOXYLIC ACID[1]

[1]Xu, G.G., C.Q. Yang and Y. Deng. 2001. Journal of Pulp and Paper Science 27(1):14-17
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ABSTRACT

Fully hydrolyzed poly(vinyl alcohol) (PVA) was applied as a co-additive of poly(maleic acid) (PMA) to improve the mechanical properties of Kraft paper. Although PMA brings about significant improvement in wet strength, it causes embrittlement and severe loss of folding endurance of treated paper. PVA is able to minimize the negative impact on dry properties of paper treated by PMA. When applied as a co-additive, PVA improves wet strength, dry strength, as well as folding endurance of the paper crosslinked by PMA. Thermal analysis data indicate that PMA reacts with PVA under the curing conditions. The improvement in mechanical properties may be attributed to the improved fiber-fiber bonding and consequently alleviation of stress concentration.

***Key words**: carboxylic acids, cellulose, crosslinking, esterification, dry strength, folding endurance, paper, poly(maleic acid), poly(vinyl alcohol), wet strength, wood pulp.*

INTRODUCTION

Polycarboxylic acids have been investigated as cellulose crosslinkers for improving the wet performance of paper [1-10]. Some multifunctional carboxylic acids of relatively small molecular sizes, such as 1,2,3,4-butanetetracarboxylic acids (BTCA) and poly(maleic acid) (PMA), bring about greatly improved wet strength at the cost of severe reduction in folding endurance of treated paper [1-3, 5-7]. In contrast, maleic acid copolymers of high molecular weight, such as poly(ethene-co-maleic acid) (PEMA) [8] and poly(methyl vinyl ether-co-maleic acid) (PMMA) [9], not only exhibit very high efficiency for improving wet strength, but also significantly improve dry strength and folding endurance of the treated paper. The improvement in dry properties of treated paper is probably a direct result of the formation of inter-fiber crosslinking, which is favored by the high molecular weight polymeric crosslinkers. However, commercial application of PMMA and PEMA appears to be not feasible due to their high cost.

Fully hydrolyzed PVA was originally used as reinforced agent for paper, and is used widely in surface sizing and pigment binding in the paper industry [10]. The object of this study is to use PMA in combination with PVA to improve wet strength and minimize its negative impact on dry properties of paper in an attempt to develop an efficient yet cost-effective crosslinking system for paper.

EXPERIMENTAL

Materials

The paper used in this research was unbleached Kraft paper with a grammage of 65g/m^2, supplied by Southwest Paper Co., Georgia. PMA with number average molecular weight of approximately 800 was a 50% aqueous solution commercially produced by FMC. NaH_2PO_2 was a reagent supplied by Aldrich. Fully hydrolyzed PVA with a viscosity of 62-72 cps was a commercial product of Air Products. Cellulose (fibrous long) was purchased from Sigma. A constant 2:1 (w/w) PMA/NaH_2PO_2 ratio was maintained for all treated solutions used in this research.

Paper Treatment

The Kraft paper sheets (25x25 cm^2) were immersed in a solution for 30 seconds, then pressed between squeezing rolls to remove the excess liquid and to reach about 95% wet pick-up. The impregnated sheets were dried on a hot plate dryer at 85^oC for 3 min to prevent curling. Each sheet was cured in a forced draft oven at a specified temperature for 1.5 min. The control sample was treated with pure water and cured at 170^oC. Five specimens were treated under each condition.

Paper Performance Testing

Dry tensile strength, wet tensile strength, and folding endurance of the treated paper sheets were evaluated according to TAPPI standard test methods T 494 om-88, T456 om-87, and T 511 om-96, respectively. For wet tensile strength, the specimens were immersed in distilled water for 24 hours before testing. Ten measurements were performed for each testing procedure. The dry strength was expressed as percentage

change over that of the control, while the wet strength was shown as the ratio of wet strength of treated paper to the dry strength of the control.

TG Measurements

A Mettler TG50 Thermobalance was used for thermal analysis of PVA, PMA and a mixture of PVA/PMA/NaH_2PO_2 at a weight ratio 2:2:1. The solid PMA was obtained by drying the PMA solution under reduced pressure. All the samples were heated from room temperature (25^{o}C) to a specified temperature at a rate of 10^{o}C/min with a continuous nitrogen flow at a rate of 10 ml/min. The sample size for the TG experiments was approximately 9 mg.

RESULTS AND DISCUSSION

Dry strength and folding endurance

Our previous research showed that treatment with PMA does not improve the dry strength of paper [5-7]. The change in the dry strength of the Kraft paper treated using 2.0% PMA with and without 1.0% PVA and cured at different temperatures is presented in Figure 4.1. One observes that treatment with PMA has little influence on the dry strength of the paper, but the dry strength increases modestly when PVA is present, particularly at lower curing temperatures (Figure 4.1). Shown in Figure 4.2 is the change in dry strength of Kraft paper treated with 2.0% PMA in combination with different amounts of PVA and cured at 170^{o}C. The data indicate that the dry strength of the crosslinked paper increases 16% when the PVA concentration increases to 3.0%. It is evident that the presence of PVA improves the dry strength of the crosslinked paper.

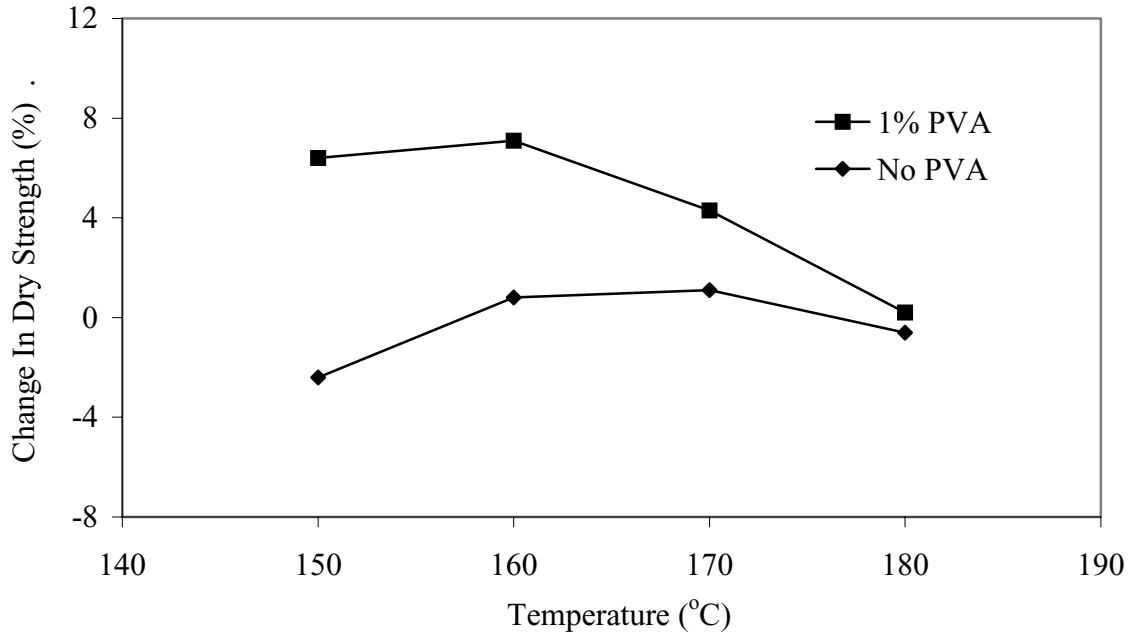

Figure 4.1. Change in dry strength of the Kraft paper treated with 2.0% PMA (with and without 1.0% PVA) and cured at different temperatures.

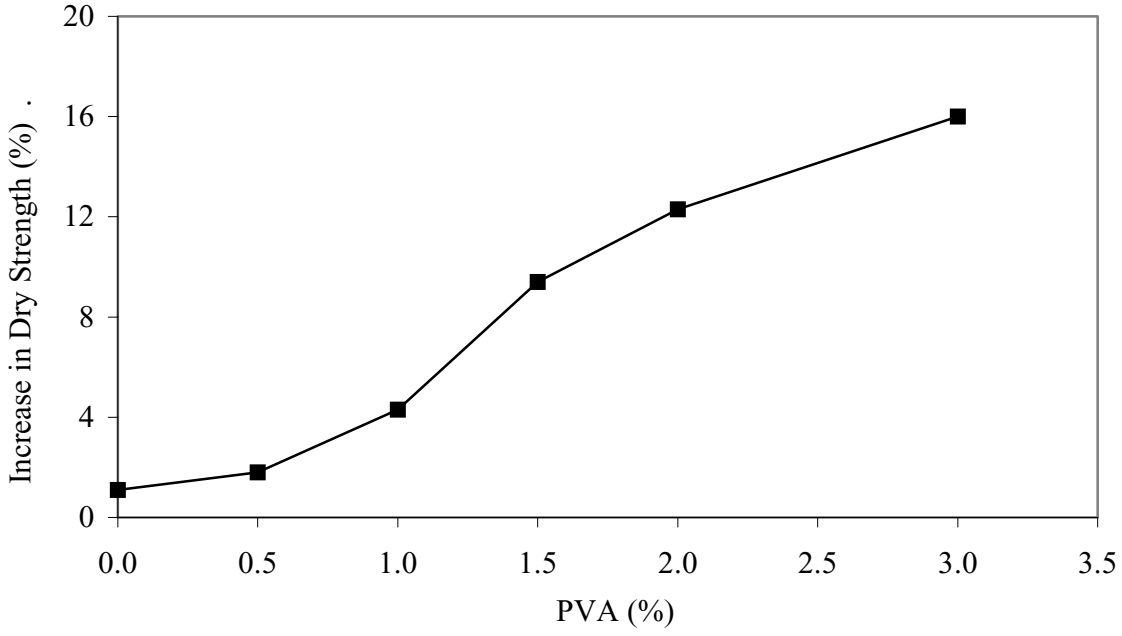

Figure 4.2. Change in dry strength of the Kraft paper treated with 2.0% PMA in combination with PVA at different concentrations and cured at 170°C.

Presented in Figure 4.3 is the folding endurance of Kraft paper treated using 2.0% PMA with and without 1.0% PVA and cured at different temperatures (150-180°C) as a function of wet strength-to-dry strength ratio (W/D) of the treated paper. The control sample has a folding endurance of 495. Treatment with PMA increases the W/D ratio but causes paper embrittlement, thus diminishing folding endurance as curing temperature increases (Figure 4.3). One observes that the folding endurance of the treated paper is increased at the same W/D levels in the entire temperature range when 1.0% PVA is present in the crosslinking system.

The folding endurance of the Kraft paper treated with 2.0% PMA in combination with different amounts of PVA and cured at 170^{o}C is plotted against the PVA concentration in Figure 4.4. The data indicate that the folding endurance increases as the PVA concentration in the crosslinking system increases. The data provide convincing evidence that the use of PVA as a co-additive improves the folding endurance of the paper crosslinked by PMA.

The improvement in dry properties can be explained by the contribution of PVA to inter-fiber bonding and stress dissipation of the fiber network. The capillary-concentration theory is applicable to the migration and distribution of non-ionic PVA in paper network [11]. High molecular weight PVA tends to stay on the fiber surface, move to crossing area and penetrate into pores and cracks on the fiber surface under the action of capillary force during drying. PVA enhances fiber-to-fiber bonding through hydrogen bonding. Moreover, PVA reacts with part of the carboxylic acid groups of PMA, thus forming long-range fiber-to-fiber crosslinkages. The fiber crossing areas are centers of stress transfer of the fiber network, while the pores and cracks are the weak points of the

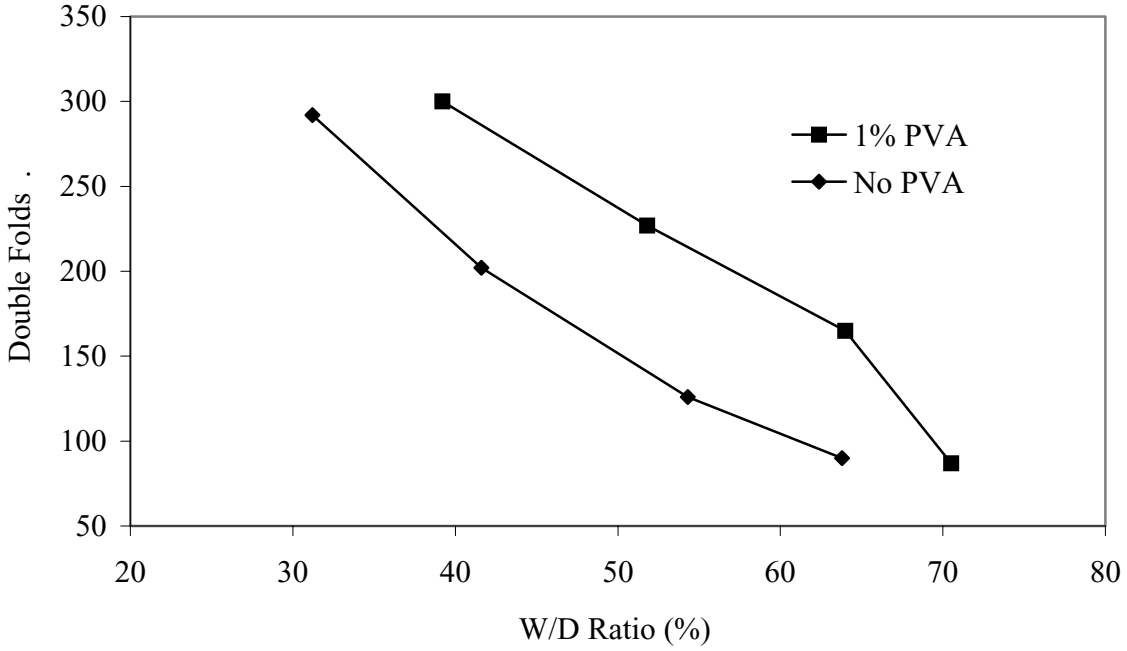

Figure 4.3. Folding endurance as a function of W/D ratio for the Kraft paper treated with 2.0%PMA (with and without 1.0% PVA) and cured at 150, 160, 170, 180^{o}C.

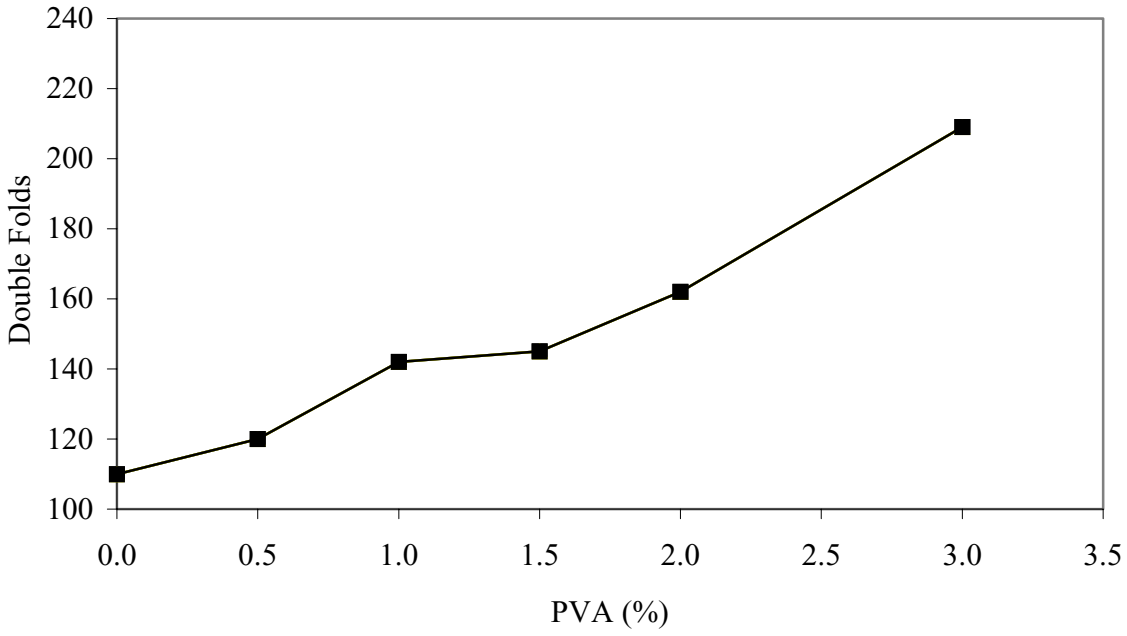

Figure 4.4. Folding endurance as a function of W/D for the Kraft paper treated with 2.0%PMA in combination with PVA at different concentrations and cured at 170^{o}C

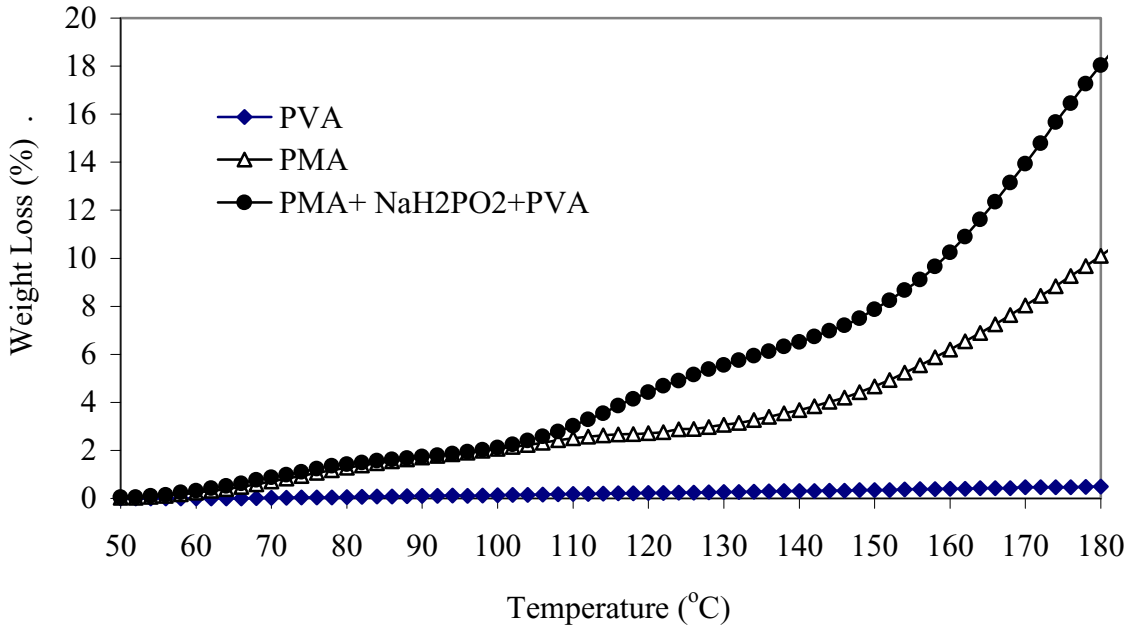

Figure 4.5. Thermogravimetric curves of PVA, PMA, and the mixture of PVA, PMA and NaH_2PO_2 at 2:2:1 weight ratio

fibers. As a result, PVA improves interfiber bonding, strengthens the weak points of fibers, and enhances the efficiency of stress transfer of the fiber network.

We used Thermal Gravimetry (TG) to confirm the hypothesis that a chemical reaction takes place between PMA and PVA under the curing conditions. Presented in Figure 4.5 are the TG curves of PVA, PMA, and a mixture of PVA, PMA and NaH_2PO_2 at a weight ratio of 2:2:1. No weight loss takes place as the temperature increases to 180°C for PVA. PMA gradually loses weight as temperature increases due to dehydration between the carboxylic acid groups and formation of a 5-membered cyclic anhydride [12]. One observes a significant increase in percent weight loss when PMA is combined with PVA and NaH_2PO_2. Thus, the TG data presented here support the hypothesis that PVA esterfies PMA under the curing conditions. Because the PVA has

an approximate molecular weight of 140,000, the reaction between PMA and PVA certainly promotes the formation of inter-fiber bonding in the treated paper.

The folding endurance of paper decreases with increasing wet strength (Figure 4.3). Our previous study found a linear relationship between the amount of ester formed on paper and the wet strength of paper crosslinked by BTCA and PMA [6]. Higher wet strength of paper as a result of the formation of a larger amount of short-range crosslinks causes more fiber enbrittlement and diminishes folding endurance. The data shown above demonstrate that the use of PVA in combination of PMA improves the folding endurance of paper crosslinked by PMA (Figure 4.3-4.4). Folding endurance is a sensitive property associated with the flexibility of paper. During the folding test, there is a gradual loosening of fiber-fiber bonds which leads to decrease of tensile strength and final fracture of paper. The addition of PVA and formation of fiber-PMA-PVA-PMA-fiber crosslinkages (instead of stiff and short linkages by PMA itself) in fiber crossing areas improve the flexibility of the crosslinked paper and provide a more efficient way of stress relaxation for the fiber network, thus improving the dry strength and folding endurance of the paper. In our previous research, it was noted that the use of high molecular weight PMMA and PEMA as the crosslinking agents for paper resulted in significantly improved folding endurance than the use of low molecular weight BTCA and PMA [8, 9].

Wet strength of the crosslinked paper

Presented in Figure 4.6 is the W/D ratio of the Kraft paper treated with 2.0% PMA and 2.0% PMA in combination with 1.0% PVA, and cured at different temperatures. One

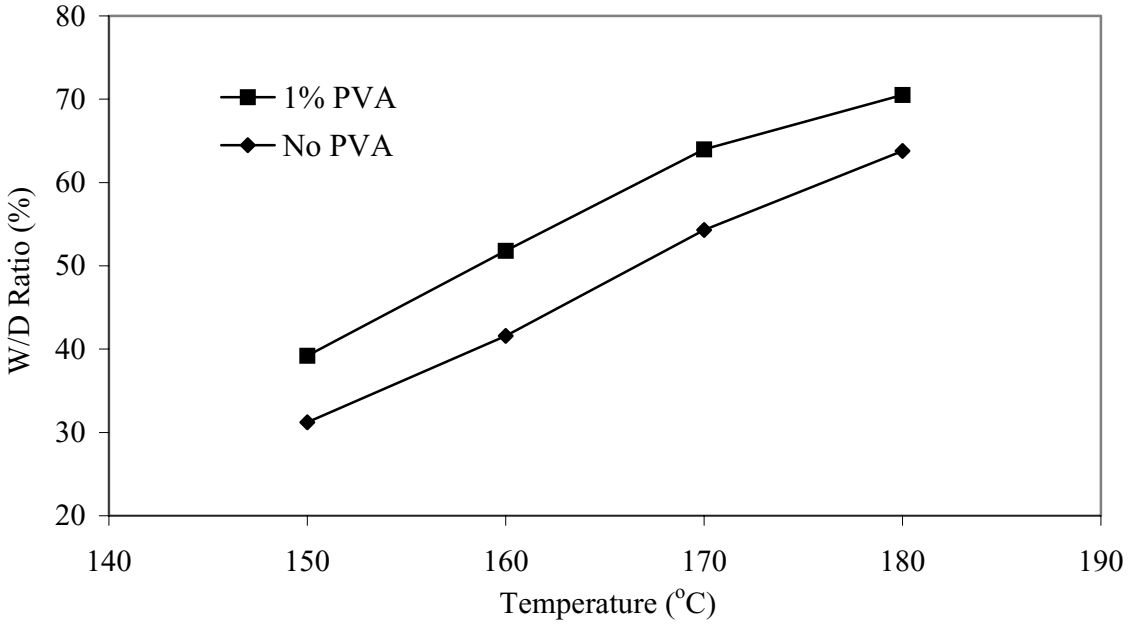

Figure 4.6. W/D ratio of the Kraft paper treated with 2.0% PMA (with and without 1.0% PVA) and cured at different temperatures

observes that W/D ratio increases as the curing temperature increases, and that the paper treated by 2.0% PMA/1.0% PVA shows approximately 10% higher W/D ratio than that treated by 2.0% PMA in the entire temperature range. It is also found that the use of 1.0% PVA in the crosslinking system increases W/D ratios by 5-10% for the paper treated with PMA of concentrations ranging from 1.0 to 4.0% and cured at 170°C (Figure 4.7). One also finds that the W/D ratio of the paper crosslinked by 2.0% PMA increases as the concentration of PVA as a co-additive increases (Figure 4.8). The data also show that increasing the PVA concentration beyond 1.0% does not result in further improvement in wet strength of paper (Figure 4.8).

There are three possible explanations for the improvement of paper wet strength by PVA. The reaction of PVA to PMA creates more efficient inter-fiber bonding through the formation of fiber-PMA-PVA-PMA-fiber bonds, thus increasing both dry and wet

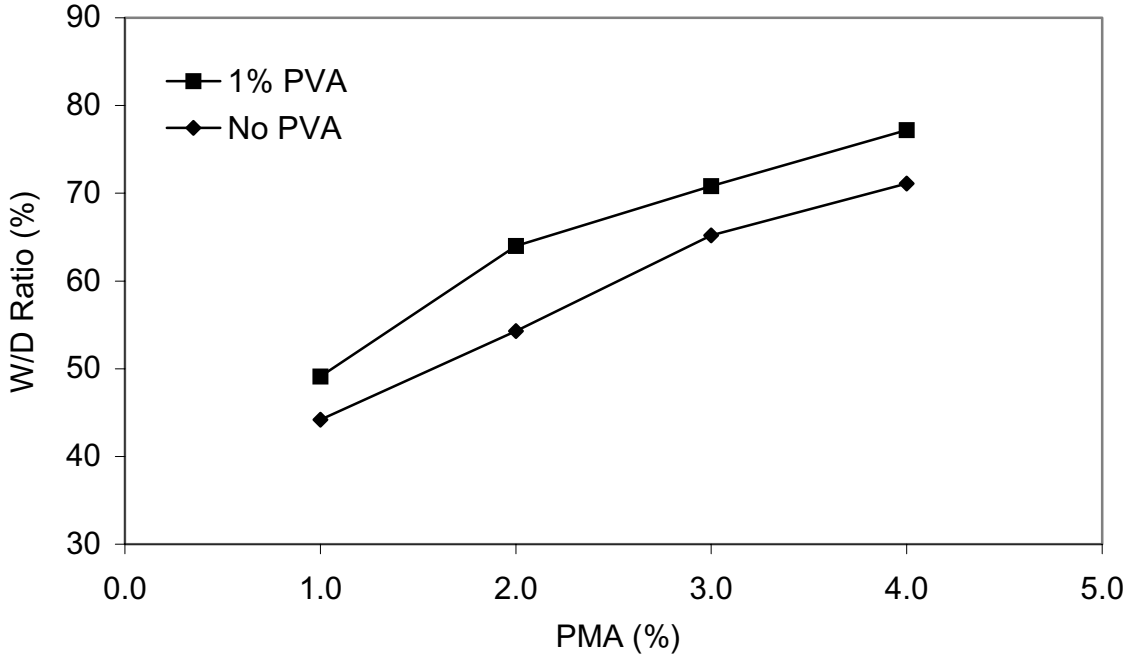

Figure 4.7. W/D ratio of the Kraft paper treated with PMA at different concentrations (with and without 1.0% PVA) and cured at 170°C.

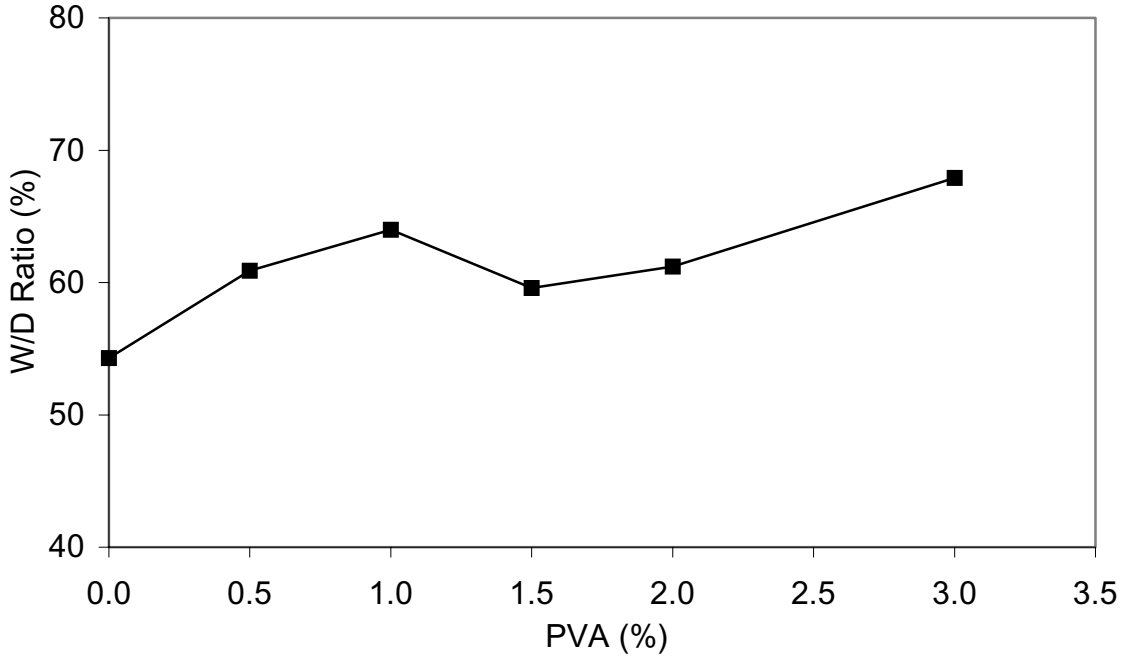

Figure 4.8. W/D ratio of the Kraft paper treated with 2.0% PMA in combination with PVA at different concentrations and cured at 170°C

strength of the treated paper. In our previous research, it was found that high molecular weight PMMA and PEMA exhibited higher efficiency for increasing paper wet strength than low molecular weight BTCA and PMA [8, 9]. Fully hydrolyzed PVA may also improve the water-resistance of paper surface. PVA may also retard the penetration of PMA into fiber interior. Consequently, more PMA stays on fiber surface and the fiber crossing areas to react with PVA, thus enhancing inter-fiber bonding.

There exists an upper concentration limit of PVA for wet strength improvement. Excess use of PVA causes little increase in wet strength. Figure 4.8 shows that addition of more than 1.0% PVA does not provide further improvement in wet strength of paper treated by 2.0% PMA. PVA itself is not reactive to cellulose. It must react with PMA to participate in the crosslinking of the cellulosic fibers, thus contributing to the enhancement of inter-fiber bonding. Due to the small molecular size and penetrating ability of PMA, only limited amount of PMA molecules is located on the fiber surface and fiber crossing area readily to react with PVA. Meanwhile, cellulose competes with PVA for the limited amount of available carboxylic acid group of PMA. Subsequently, the capacity of PVA for participating in crosslinking of cellulose is limited to a certain extent. This is the possible reason why wet strength of the paper crosslinked by 2.0% PMA does not increase further when more than 1.0% PVA is used in the system as shown in Figure 4.8.

CONCLUSION

The use of PVA as a co-additive enhances the performance of PMA as a wet-strength agent of paper. The addition of PVA provides significant improvement in dry strength, wet strength, as well as folding endurance of the paper crosslinked by PMA. This is probably due to the enhancement of fiber-to-fiber bonding by the reaction between PMA and the high molecular weight PVA.

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CHAPTER 5

APPLICATION OF BIFUNCTIONAL ALDEHYDES TO IMPROVE PAPER WET STRENGTH[1]

[1]Xu, G.G. and C.Q Yang. 2001. Accepted by Journal of Applied Polymer Science
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ABSTRACT

Glyoxal and glutaraldehyde behave very differently for improving wet strength of paper. It is found that glyoxal is very efficient for improving temporary wet strength of paper without presence of a catalyst and exposure to elevated temperatures. When a metal salt, such as $Zn(NO_3)_2$, is used as a catalyst and curing temperature is increased, the durable wet strength of glyoxal-treated paper increases at the expense of its flexibility as shown by reduced stretch and folding endurance. Glutaraldehyde is not able to provide any improvement in wet strength to paper even under high curing temperature, provided no catalyst is used. With the aid of a metal salt catalyst, glutaraldehyde imparts excellent durable wet strength to paper without significantly sacrificing folding endurance, and the wet strength of glutaraldehyde-treated paper increases in proportional to the curing temperature. The different behavior of glyoxal and glutaraldehyde may be attributed to their different reactivity toward cellulose.

INTRODUCTION

Environmental consideration has been the driving force for the papermaking industry to develop new wet-strength resins without the emission of carcinogenic formaldehyde and adsorbable organic halides (AOX) [1]. Polycarboxylic acids have been investigated for enhancing the wet performance of paper [2-11]. Among the carboxylic acids of relative small molecular sizes, 1,2,3,4-butanetetracarboxylic acids (BTCA) and poly(maleic acid) (PMA) were the most effective crosslinking agents [5,7]. However, the treatment with BTCA and PMA causes paper embrittlement, thus severely reducing its folding endurance.

We have discovered two approaches to improve flexibility of the paper crosslinked by polycarboxylic acids [9,10,11]. We treated paper with high molecular weight maleic acid copolymers, including poly(ethene-co-maleic acid) and poly(methyl vinyl ether-co-maleic acid) [9,10], and found that the high molecular weight maleic acid copolymers not only exhibit higher efficiency for improving wet strength but also significantly improve the dry strength and folding endurance of the treated paper. To improve the cost effectiveness of the treatment, we used poly(maleic acid) in combination with poly(vinyl alcohol) to treat kraft paper and found that the use of poly(vinyl alcohol) as a co-additive notably improves the dry strength, folding endurance as well as wet strength of treated paper [11]. However, the use of polycarboxylic acids requires a curing temperature as high as 170^{o}C for effective crosslinking, which is beyond the operating temperature range of current papermaking machines.

In the past, bifunctional aldehydes were studied as crosslinking agents of cellulose to impart wrinkle resistance of cotton fabric [12-14]. The multifunctional aldehydes

include glyoxal, glutaraldehyde, succinaldehyde, and their acetal derivatives. The reaction between dialdehydes and cellulose is catalyzed by metal or ammonium salts [15,16]. The most frequently used catalysts include aluminum, magnesium, and zinc salts of inorganic acids [16]. Glyoxal was also used to provide temporary wet strength for paper [17, 18, 19]. These multifunctional aldehydes enjoy the advantage of low curing temperatures (around 120^{o}C), which is consistent to the current papermaking condition.

The object of this study is to evaluate the feasibility of using glyoxal and glutaraldehyde as wet strength agents for paper.

EXPERIMENTAL

Materials

An unbleached kraft paper with a grammage of 65g/m^2 was used in this research. Glutaraldehyde was a 50% aqueous solution. Glyoxal was a 40% aqueous solution. $Zn(NO_3)_2$ was a regent grade chemical. The aldehyde-to-$Zn(NO_3)_2$ ratios (w/w) in all solutions were 1.16 :0.758 for glyoxal and 2.0:0.758 for glutaraldehyde. The pH of all solutions was adjusted to 4.3 with NaOH and citric acid.

Paper Treatment

The kraft paper sheets (25x25 cm^2) were immersed in a solution for 30 seconds, then pressed between squeezing rolls to remove the excess liquid to reach about 90% wet pick-up. The impregnated sheets were dried on a hot plate dryer at 85^{o}C for 3 min to prevent curling. Each sheet was cured in a force draft oven at specified temperatures for 1.5 min. The control sample was the paper subjected to the same treating procedure except using deionized water instead of a solution. Five specimens were treated under each condition.

Paper Performance Testing

Dry tensile strength, wet tensile strength, and folding endurance of the treated paper sheets were evaluated according to TAPPI standard test methods T 494 om-96, T456 om-87, and T 511 om-96, respectively. For wet tensile strength, the specimens were immersed in deionized water for 10 min, 2 hours, or 24 hours before testing. Ten measurements were performed for each testing procedure.

The wet strength (W/D ratio) was defined as ratio of the wet strength of treated paper to the dry strength of control sample. The dry strength and stretch were expressed as percentage changes over those of control sample. The folding endurance is expressed as the number of double fold before the specimen breaks. The properties of control sample were shown as footnote under Table 1.

RESULTS AND DISCUSSION

Properties of the paper treated with dialdehydes without a catalyst

The kraft paper sheets were treated with 1.16% (0.20 mol/L) of glyoxal without using a catalyst, and cured at different temperatures for 1.5 min. The cured paper was then soaked in water for different lengths of time before its wet strength was tested. The wet-to-dry strength ratios (W/D) of the treated kraft paper are presented in Figure 5.1. One observes that different curing temperatures did not result in significantly different wet strength of treated paper. All samples cured at temperatures ranging from 110 to 140^{o}C exhibited wet strength similar to those without curing. All treated paper samples showed high levels of wet strength with W/D ratios around 40% after being soaked in water for 10 minutes, but the wet strength deteriorated quickly as the soaking time was

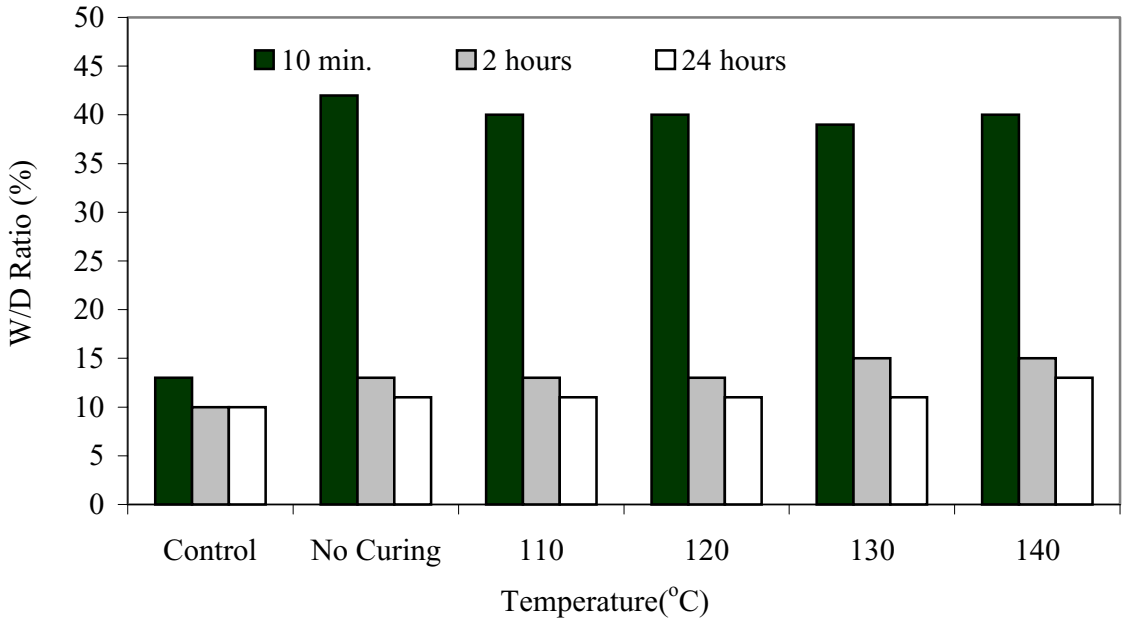


Figure 5.1. Wet strength of the paper treated with 1.16% (0.20 mol/L) glyoxal without a catalyst after being soaked in water for 10 min, 2 hours and 24 hours

increased. The W/D ratio decreased to 10-15% after being soaked in water for 2 hours (Figure 5.1). The wet strength of the treated paper cured under different temperatures was close to that of the control sample after being soaked for 2 hours. It indicates that the glyoxal-treatment without a catalyst imparts only temporary wet strength to the paper.

The wet strength of glyoxal-treated paper is a result of the crosslinking of cellulose by glyoxal. Glyoxal is able to react with hydroxyl groups of cellulose to form hemiacetal bonds between cellulose molecules [20]. The improved wet strength of the glyoxal-treated paper without curing suggests that the hemiacetals form so easily as the water is removed from the treated paper during the drying process that further curing is not needed. The hemiacetal bonds produced by glyoxal between cellulose molecules,

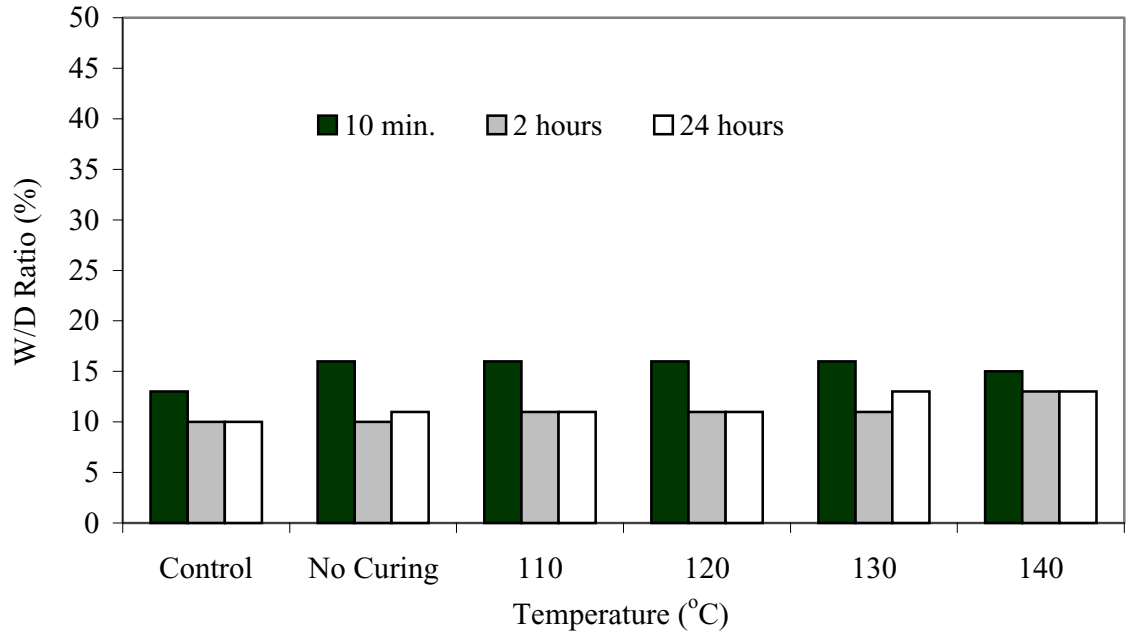


Figure 5.2. Wet strength of the paper treated with 2.0% (0.20 mol/L) glutaraldehyde without a catalyst after being soaked in water for 10 min, 2 hours and 24 hours

however, are sensitive to water and can be replaced by hemiacetal bonds with water when the paper is saturated by water for a short period of time. Consequently, the wet strength imparted by glyoxal is only temporary.

Figure 5.2 shows the wet strength of paper treated by 2.0% (0.20 mol/L) glutaraldehyde without the use of a catalyst. The initial wet strength of paper treated by glutaraldehyde was around 15% compared with 40% for the glyoxal-treated paper. Similar to the case of glyoxal treatment, different curing temperatures have little impact on the wet strength of treated paper. The wet strengths of the paper cured under different temperatures after soaking for different lengths of time were similar to those of the control sample. Apparently, glutaraldehyde did not provide significant improvement in the wet strength of paper. The results indicate that glutaraldehyde possesses low reactivity toward cellulose even at high temperatures if no catalyst is present. The

difference in reactivity between glyoxal and glutaraldehyde may be due to the fact that the carbonyl groups in glyoxal are more electron deficient than those in glutaraldehyde. The hemiacetals are easily formed and relatively stable for those aldehydes whose carbonyl group is strongly electron deficient [20].

The dry properties of the paper treated by glyoxal and glutaraldehyde are shown in Table 5.1. The data show no significant change in dry strength after the chemical treatment with both glyoxal and glutaraldehyde. However, the dialdehyde treatment does reduce the dry stretch, particularly in the case of glyoxal. The treatment by glyoxal causes much more reduction in stretch than that by glutaraldehyde. The high loss of stretch of sample treated by glutaraldehyde and cured at 140^{o}C may be due to unexpected experimental error or sample handling. The reduction of stretch is possibly a result of crosslinking between the cellulose molecules. The short linkage between cellulose molecules produced by glyoxal limits the mobility of cellulose molecules and thus reduces the stretch of paper network. The reduced stretch is also consistent with the decreased folding endurance. The short and rigid crosslinkage reduces the flexibility of paper and diminishes the folding endurance. Consequently, paper treated with glyoxal showed more significant loss of stretch and folding endurance than that treated with glutaraldehyde.

Properties of the paper treated with dialdehydes with $Zn(NO_3)_2$ as a catalyst

The wet strength of the paper treated with 1.16% (0.20 mol/L) of glyoxal and 0.758% $Zn(NO_3)_2$ and cured at different temperatures are shown in Figure 5.3. The data indicate that the initial wet strength (after being soaked in water for 10 min) of the treated

Table 5.1 Dry properties of kraft paper treated by 1.16% glyoxal (0.20 mol/L) and 2.0% glutaraldehyde (0.2 mol/L) without a catalyst, cured at different temperatures

Dialdehyde	Temperature (^{o}C)	Change in Dry Strength (%)	Change in Stretch (%)	Folding Endurance (times)
Glyoxal	No Curing	6.5	-20.1	386
	110	6.5	-17.4	387
	120	4.8	-15.6	476
	130	0	-19.4	439
	140	1.6	-14.1	334
Glutaraldehyde	No Curing	-3.2	-3.5	495
	110	-4.8	-5.4	469
	120	1.6	-5.2	418
	130	0	-3.9	439
	140	-1.6	-10.6	452

Note: For control sample, W/D=9.8%, Dry Strength=4.11 kN/m, Stretch=7.6%, Folding Endurance=489 times

paper is independent of curing temperatures. The wet strengths were slightly lower than those of paper treated with glyoxal of the same concentrations without a catalyst as shown in Figure 5.1. The wet strength after being soaked in water for 2 hours and 24 hours, however, increased gradually as curing temperature was increased. The W/D ratio after 24 hours' soaking increased from 13% at 110^{o}C to 24% at 140^{o}C. It means that the wet strength becomes more durable at higher curing temperatures. It is well known that aldehyde reacts with hydroxyl group to form acetal under catalysis of Lewis acids [20]. Acetal is stable under neutral and alkaline conditions. The data show that high curing temperature increases reaction rate and shifts the reaction equilibrium to the direction of acetal formation.

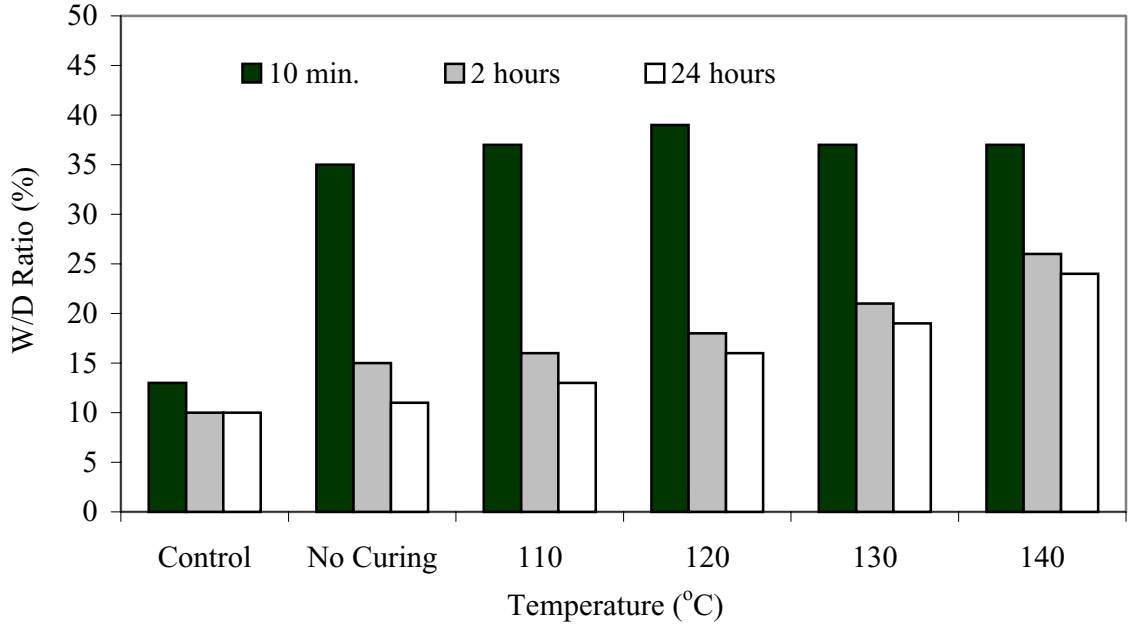


Figure 5.3. Wet strength of the paper treated with 1.16% (0.20 mol/L) glyoxal and 0.758% $Zn(NO_3)_2$ after being soaked in water for 10 min, 2 hours and 24 hours

The wet strength of kraft paper treated by 2.0% (0.20mol/L) glutaraldehyde and 0.758% $Zn(NO_3)_2$ and cured at different temperatures is illustrated in Figure 5.4. There are two major differences between glyoxal and glutaraldehyde. The first is that the wet strength of glutaraldehyde-treated paper is more durable than that of glyoxal-treated paper at all curing conditions. For the glutaraldehyde-treated paper, its W/D ratios remained almost unchanged during 24-hour's soaking in water. The second difference is that the wet strength increased steadily as the curing temperature was raised from 110 to 140°C. The W/D ratio after 24-hour soaking increased from 15% at 110°C to 50% at 140°C (Figure 5.4), which is much greater in magnitude than that of glyoxal-treated paper as shown in Figure 5.3.

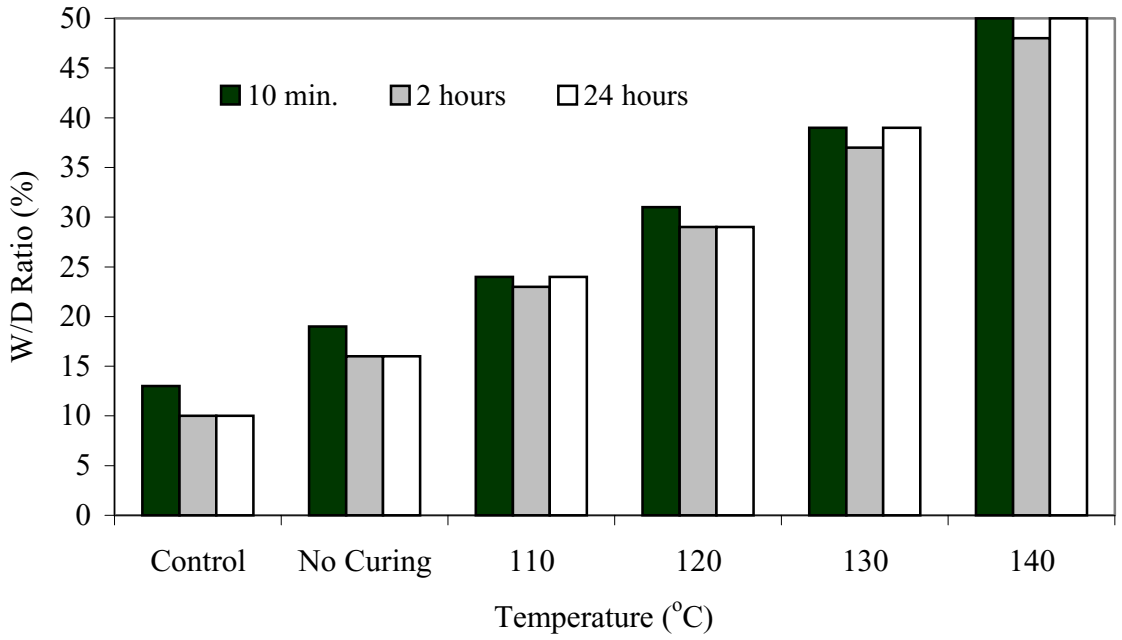


Figure 5.4. Wet strength of the paper treated with 2.0% (0.20 mol/L) glutaraldehyde and 0.758% $Zn(NO_3)_2$ after being soaked in water for 10 min, 2 hours and 24 hours

The wet strength of the paper treated with a bifunctional aldehyde increased steadily as the concentration of the dialdehydes was increased (Figure 5.5). At the same concentrations, glutaraldehyde is much more efficient for improving wet strength of paper than glyoxal. When the concentration exceeded 0.20 mol/L, the glutaraldehyde-treated paper showed a W/D ratio more than twice that of glyoxal-treated paper. One also observes a leveling-off effect as the concentration reaches 0.50 mol/L (Figure 5.5).

The significantly improved wet strength is possibly a result of the formation of acetal crosslinkages between cellulose molecules by glutaraldehyde. The acetal formation is strongly affected by steric and conformational factors [20]. As

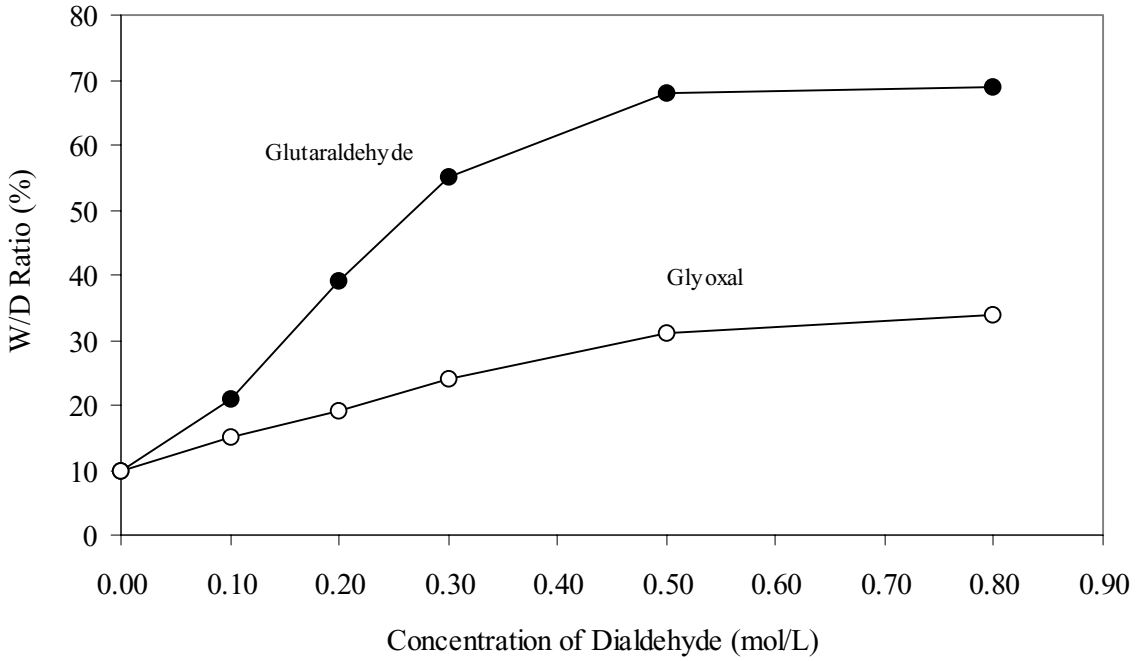
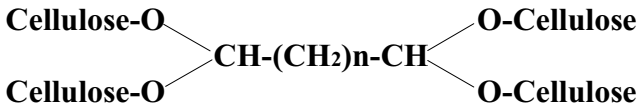


Figure 5.5. Wet strength (24 hours' soaking) of the paper treated with glyoxal and glutaraldehyde of different concentrations and $Zn(NO_3)_2$, and cured at 130°C

demonstrated in Scheme 1, one glutaraldehyde molecule may react with four cellulose hydroxyl groups by acetalization. For glyoxal, however, the two aldehyde groups are too close to each other to allow them to reach cellulosic hydroxyl groups to form crosslinkages.



Glyoxal: n = 0
Glutaraldehyde: n = 3

Scheme 1 Acetalization of cellulose by dialdehyde

Table 5.2 Dry properties of kraft paper treated by 1.16% (0.20mol/L) glyoxal and 2.0% (0.20 mol/L) glutaraldehyde with 0.758% $Zn(NO_3)_2$ as catalyst, cured at different temperatures

Dialdehyde	Temperature (^oC)	Change in Dry Strength (%)	Change in Stretch (%)	Folding Endurance (times)
Glyoxal	No Curing	1.6	-10.8	398
	110	3.2	-17.4	275
	120	1.6	-15.2	331
	130	1.6	-14.6	289
	140	-4.8	-16.7	174
Glutaraldehyde	No Curing	1.6	0.7	474
	110	-1.6	-8.4	429
	120	4.8	-9.8	454
	130	4.8	-16.9	434
	140	-4.8	-23.9	231

The dry properties of paper treated by 1.16% (0.20 mol/L) glyoxal and 2.0% (0.2 mol/L) glutaraldehyde are listed in Table 5.2. The dry strength remained statistically unchanged. The stretch was significantly reduced, particularly for the glyoxal-treated paper. This phenomenon is similar to that of paper treated with polycarboxylic acids of small molecular sizes [3, 4, 7, 8, 10]. The reduction of stretch is shown as a function of wet strength (after 24 hours' soaking) in Figure 5.6. At the same wet strength levels, the paper treated with glyoxal showed worse reduction in stretch than that treated with glutaraldehyde. The relatively higher loss of stretch may also be attributed to the shorter crosslinkage formed by glyoxal than by glutaraldehyde. Shorter crosslinkage is more effective in restraining the mobility of cellulose molecules, thus increasing heterogeneity of fiber network and brittleness of paper sheet.

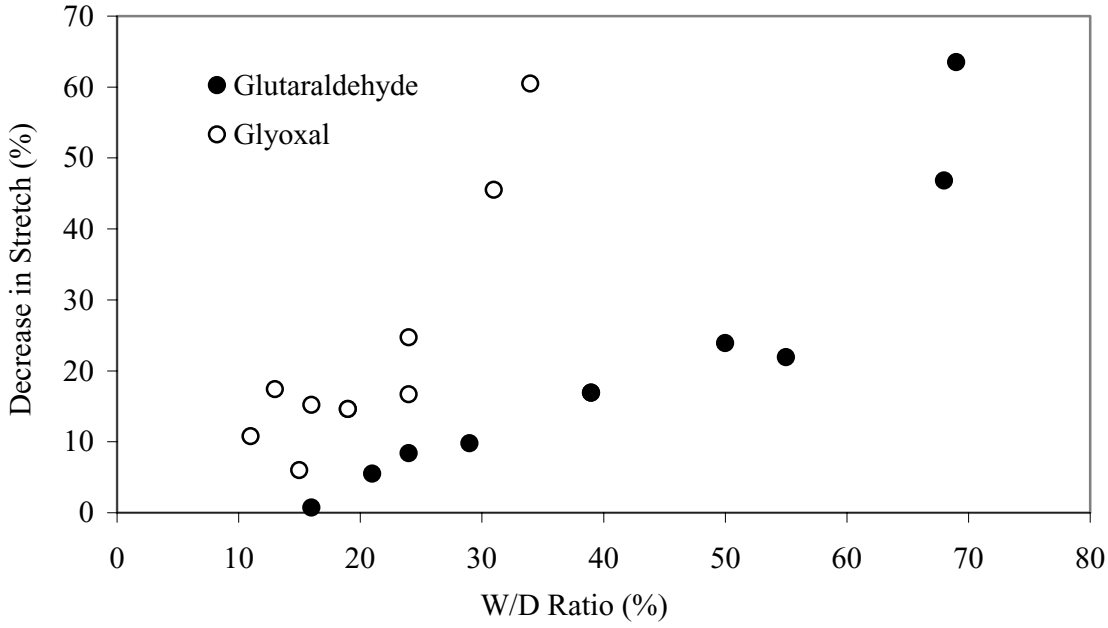


Figure 5.6. Decrease in stretch as a function of W/D ratio (24 hours' soaking) of the paper treated with glyoxal and glutaraldehyde, $Zn(NO_3)_2$ used as catalyst

One disadvantage for wet strength agents of small molecular sizes is their adverse impact on the folding endurance of treated paper. The folding endurance of paper treated with glyoxal and glutaraldehyde is presented as a function of W/D in Figure 5.7. The glyoxal-treated paper reduced its folding endurance to zero at a W/D ratio of approximately 34%, while the glutaraldehyde-treated paper still maintained its original folding endurance at a W/D ratio of approximately 40%. When W/D ratio exceeded 40%, the folding endurance decreased gradually to zero at a W/D ratio of 68%.

Folding endurance is the ability of paper to resist breaking when folded under load. It is related to the flexibility of paper [21]. Lack of adequate foldability can be result of lack of fiber length, inadequate fiber bonding, or brittleness of paper. Crosslinking of cellulose increases the brittleness of paper sheet. The reasons why glyoxal-treated paper

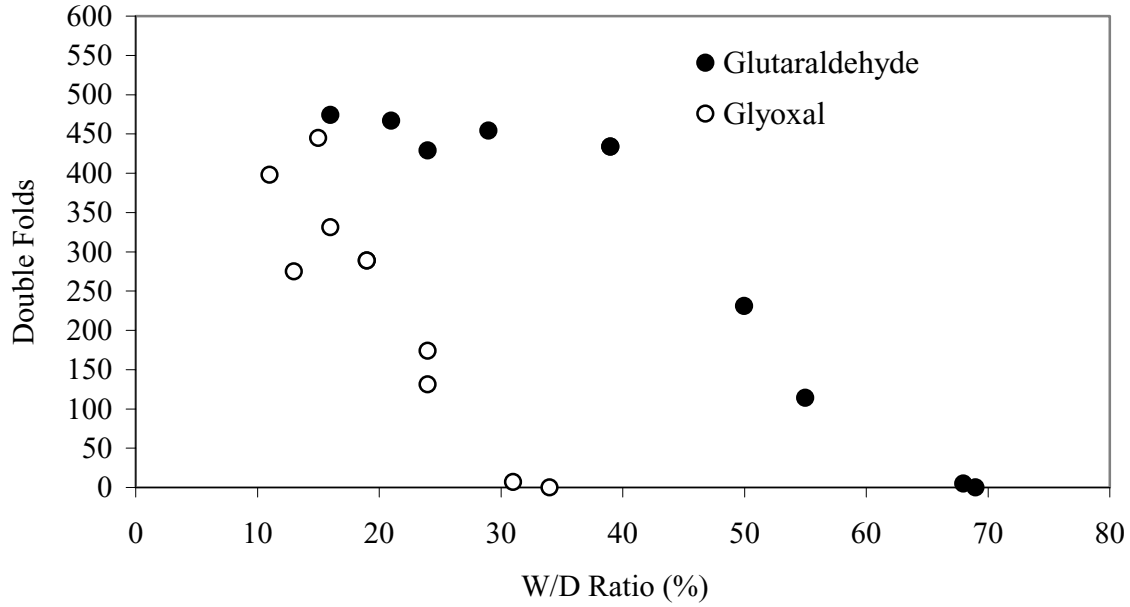


Figure 5.7. Folding endurance as a function of W/D ratio (24 hours' soaking) of the paper treated with glyoxal and glutaraldehyde, $Zn(NO_3)_2$ used as catalyst.

exhibits lower folding endurance than glutaraldehyde-treated paper are similar to those for the difference in loss of stretch as discussed above.

CONCLUSION

Glyoxal and glutaraldehyde show significantly different reactivity toward cellulose and thus their ability to improve wet strength of paper. Glyoxal is able to react with cellulose without use of a catalyst and elevated temperatures to provide temporary wet strength to paper. The use of $Zn(NO_3)_2$ as a catalyst improves the durability of the crosslinkage formed by glyoxal to some extent, but it also causes severe embrittlement and loss of folding endurance of the treated paper.

Without a catalyst, glutaraldehyde is not able to impart any wet strength to paper even under elevated curing temperatures. In the presence of a catalyst such as $Zn(NO_3)_2$,

glutaraldehyde is very efficient in crosslinking cellulose and thus improving paper wet strength. Glutaraldehyde is also able to retain stretch and folding endurance of the treated paper as wet strength is developed. Compared to the paper treated with glyoxal, the paper treated with glutaraldehyde exhibits both higher level of wet strength and higher retention of its flexibility.

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CHAPTER 6

APPLICATION OF GLUTARALDEHYDE AND POLY(VINYL ALCOHOL) TO IMPROVE PAPER STRENGTH[1]

[1]Xu, G.G. and C.Q. Yang. 2001. Tappi Journal 84(6)

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ABSTRACT

Glutaraldehyde in combination with fully hydrolyzed poly(vinyl alcohol) (PVA) is applied to improve dry and wet performance of kraft paper. The properties of the paper crosslinked by glutaraldehyde alone and by the combination of glutaraldehyde and PVA are compared. Glutaraldehyde alone improves wet strength of paper at the expense of its flexibility, thus diminishing stretch, tensile energy absorption and folding endurance. Combining PVA as a co-additive with glutaraldehyde not only improves the wet strength but also brings about significant increase in dry strength, tensile energy absorption, and folding endurance of treated paper. The improvement in mechanical properties of the crosslinked paper is probably attributed to the improved fiber-to-fiber bonding by linkages of cellulose-glutaraldehyde-PVA-glutaraldehyde-cellulose.

INTRODUCTION

The paper industry is currently seeking environment-friendly alternative wet-strength resins because of the emission of carcinogenic formaldehyde and adsorbable organic chlorides (AOX) by the conventional resins [1]. Ester crosslinking of cellulose using polycarboxylic acids has been investigated for modifying wet performance of paper [2, 3, 4]. Among all multifunctional carboxylic acids studied, 1,2,3,4-butanetetracarboxylic acids (BTCA) was the most effective crosslinking agent [5]. We applied poly(maleic acid) (PMA) as a cost-effective alternative, and found that PMA is equally efficient for improving wet performance of paper [6, 7, 8]. However, the treatment with BTCA, PMA, or other polycarboxylic acids of relatively small molecular sizes causes severe paper embrittlement. The improvement in wet strength is achieved at the expense of its folding endurance.

We also used high molecular weight maleic anhydride copolymers, such as poly(ethene-co-maleic anhydride) [9] and poly(methyl vinyl ether-co-maleic anhydride) [10], to improve the wet performance of paper. We found that the high molecular weight polycarboxylic acids not only exhibit higher efficiency for improving wet strength but also significantly improve the dry strength and folding endurance of treated paper. We believed that the high molecular weight crosslinkers tend to produce more interfiber crosslinks, thus facilitating the stress dissipation of paper network, whereas small size crosslinkers produce predominantly intrafiber crosslinks [9, 10].

Effective ester crosslinking using a polycarboxylic acid requires curing temperatures around 170^{o}C, which is well above the paper machine temperatures. We evaluated dialdehydes as wet strength agents of paper, and found that glutaraldehyde is

very effective in improving durable wet strength of paper at relatively lower temperatures [11]. Glyoxal was used to provide temporary wet strength for paper 30 years ago [12, 13]. Dialdehydes, similar to BTCA and other polycarboxylic acids of small sizes, causes serious paper embrittlement. On the other hand, multifunctional aldehydes crosslink cellulose at lower curing temperatures (around 120^{o}C), which is consistent with the current papermaking conditions.

Fully hydrolyzed polyvinyl alcohol (PVA) is a polymer with high tensile strength, excellent flexibility, good water resistance, and outstanding binding capacity [14]. We used PVA in combination with PMA to improve wet strength of paper, and found that the addition of PVA significantly improves the wet strength, dry strength, and folding endurance of paper crosslinked by PMA [15].

The objective of this study is to use glutaraldehyde in combination with PVA to improve the wet strength, dry strength and folding endurance of paper in an attempt to develop an efficient yet cost-effective wet strength agent, which does not require high curing temperatures.

EXPERIMENTAL

Materials

The paper used in this research was unbleached kraft paper with grammage of 65g/m^2. Glutaraldehyde was a 50% aqueous solution. Catalyst 531 was a durable press catalyst system of 30% solid consisting of $MgCl_2$ and citric acid. Fully hydrolyzed PVA had a viscosity of 62-72 cps. A constant 1:0.45 glutaraldehyde/catalyst (w/w, based on products) was maintained for all treating solutions.

Paper Treatment

The kraft paper sheets with a size of 25x25 cm^2 were immersed in a solution for 30 seconds, then pressed between squeezing rolls to remove the excess liquid and to reach about 95% wet pick-up. The impregnated sheets were dried on a hot plate dryer at 85^oC for 3 min to prevent curling. Each sheet was cured in a force draft oven at specified temperatures for 1.5 min. The cured sheets were rinsed in running water for 15 minutes to remove unreacted chemicals, and then dried. The control sample was treated with pure water and cured at 130^oC. Five specimens were treated under each condition.

Paper Performance Testing

Dry tensile strength, wet tensile strength, and folding endurance of the treated paper sheets were evaluated according to TAPPI standard test methods T 494 om-88, T456 om-87, and T 511 om-96, respectively. For wet tensile strength, the specimens were immersed in distilled water for 24 hours before testing. Ten measurements were performed for each testing procedure.

The dry strength, stretch, and tensile energy absorption were expressed as percentage changes over those of control sample. The wet strength (W/D ratio) was expressed as ratio of wet strength of treated paper to the dry strength of control sample.

RESULTS AND DISCUSSION

Dry Strength and Tensile Energy Absorption

The changes in dry strength, stretch and tensile energy absorption (TEA) of the kraft paper treated with 2.0% glutaraldehyde and 2.0% glutaraldehyde in combination with 1.0% PVA and cured at different temperatures are presented in Figure 6.1, 6.2, and 6.3, respectively. One observes that treatment with glutaraldehyde has little influence on the dry strength of the paper, and it causes approximately 20% reduction in stretch, and 10-20% loss in tensile energy absorption. The result indicates that treatment with glutaraldehyde causes serious paper embrittlement and reduces its extensibility. In contrast, treatment by combination of 2.0% glutaraldehyde and 1.0% PVA brings about 15-20% increases in both dry strength and tensile energy absorption without apparent affect on stretch.

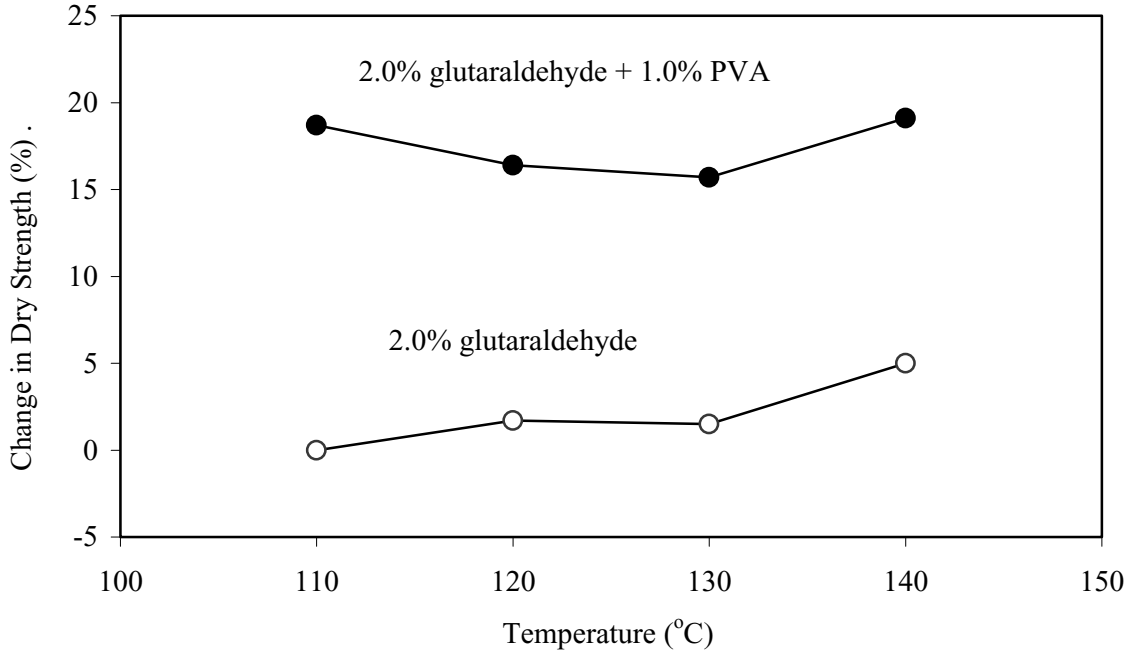

Figure 6.1. Change in dry strength of kraft paper treated with 2.0% glutaraldehyde with and without 1.0% PVA, cured at different temperatures

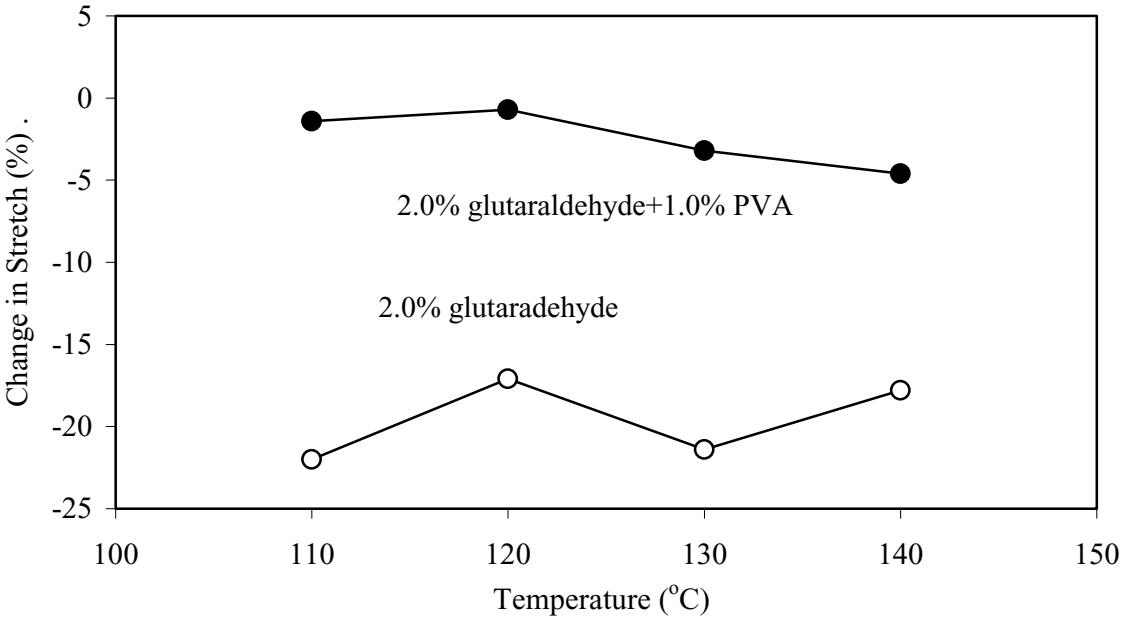

Figure 6.2. Change in stretch of paper treated with 2.0% glutaraldehyde with and without 1.0% PVA, cured at different temperatures

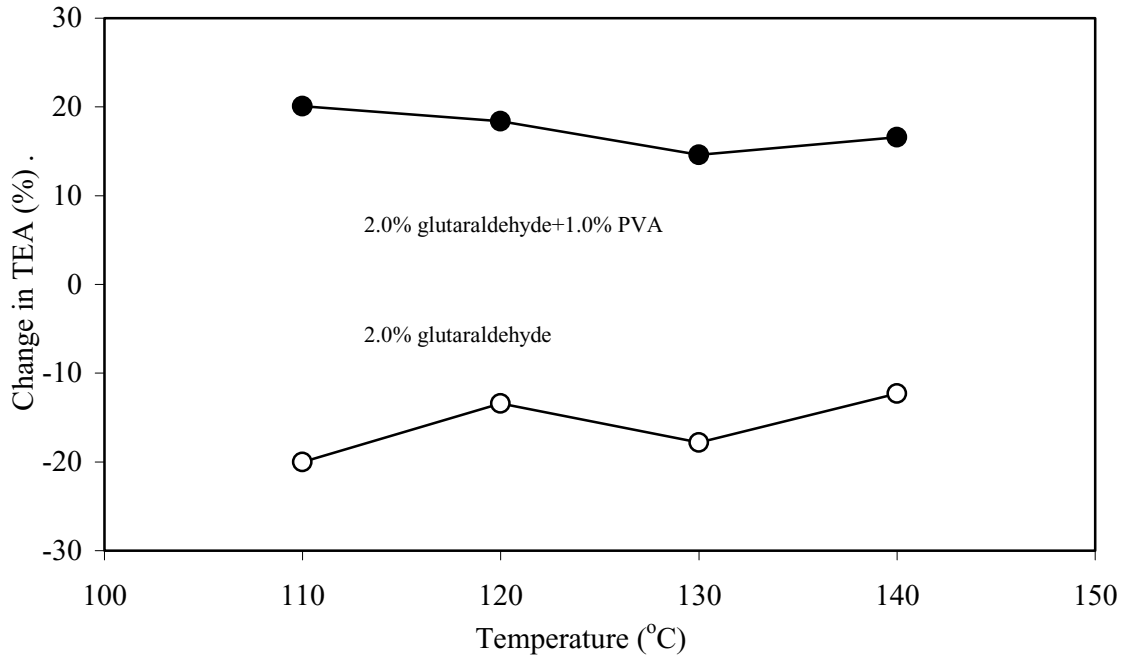

Figure 6.3. Change in tensile energy absorption (TEA) of paper treated with 2.0% glutaraldehyde with and without 1.0% PVA, cured at different temperatures

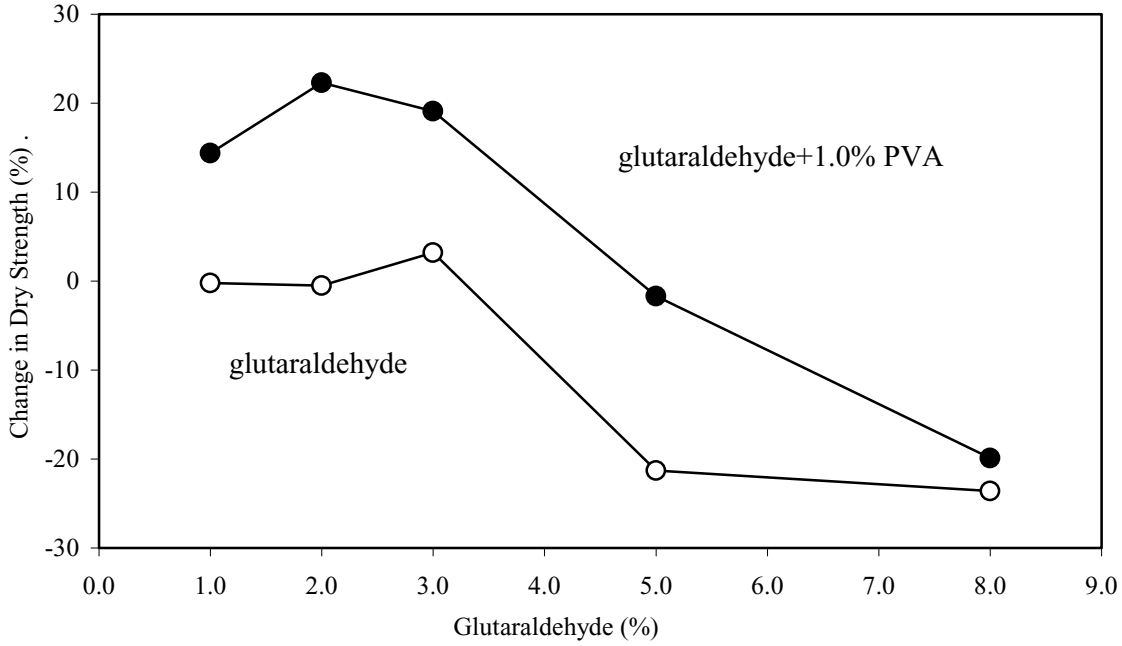

Figure 6.4. Change in dry strength of paper treated with different amounts of glutaraldehyde with and without 1.0% PVA, cured at 130^{o}C

The change in dry strength and tensile energy absorption of kraft paper treated with different amounts of glutaraldehyde with and without 1.0% PVA and cured at 130^{o}C for 1.5 min are shown in Figures 6.4 and 6.5, respectively. In the case of no PVA addition, glutaraldehyde causes severe reduction in dry strength when glutaraldehyde level exceeds 3.0% (Figure 6.4). More drastic change exists for TEA (Figure 6.5). TEA decreases very quickly as the glutaraldehyde concentration is increased. The use of 5.0% glutaraldehyde results in more than 70% loss in tensile energy absorption. It is also evident that combining glutaraldehyde with PVA significantly improves dry performance of paper. The use of 1.0% PVA brings about 15-20% increase in dry strength and TEA of the treated paper.

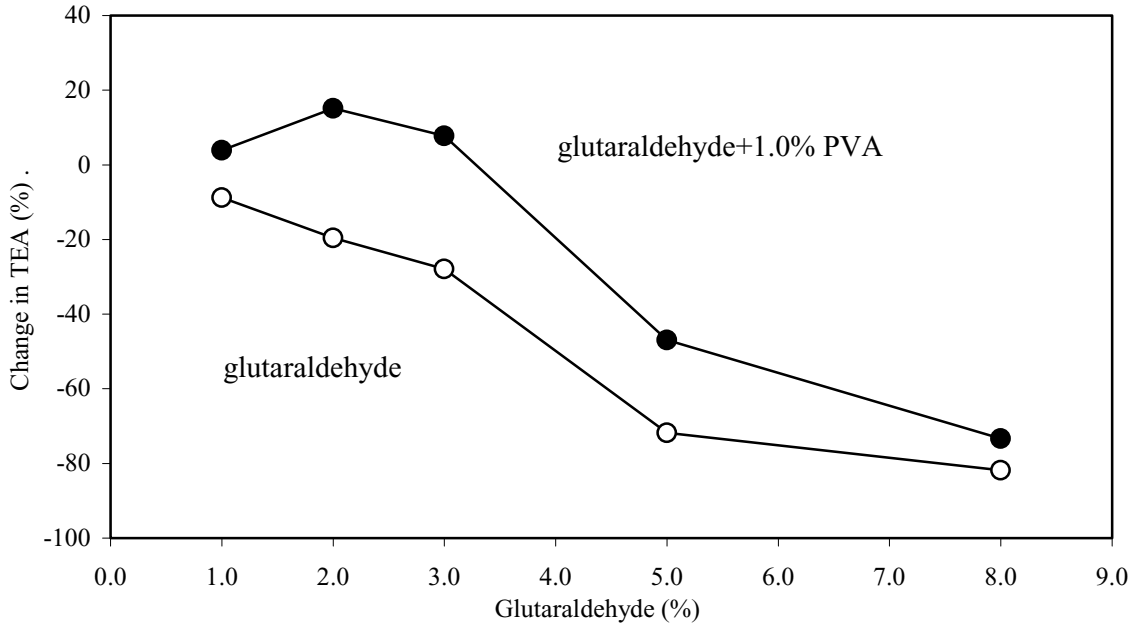

Figure 6.5. Change in tensile energy absorption (TEA) of paper treated with different amounts of glutaraldehyde with and without 1.0% PVA, and cured at 130^{o}C

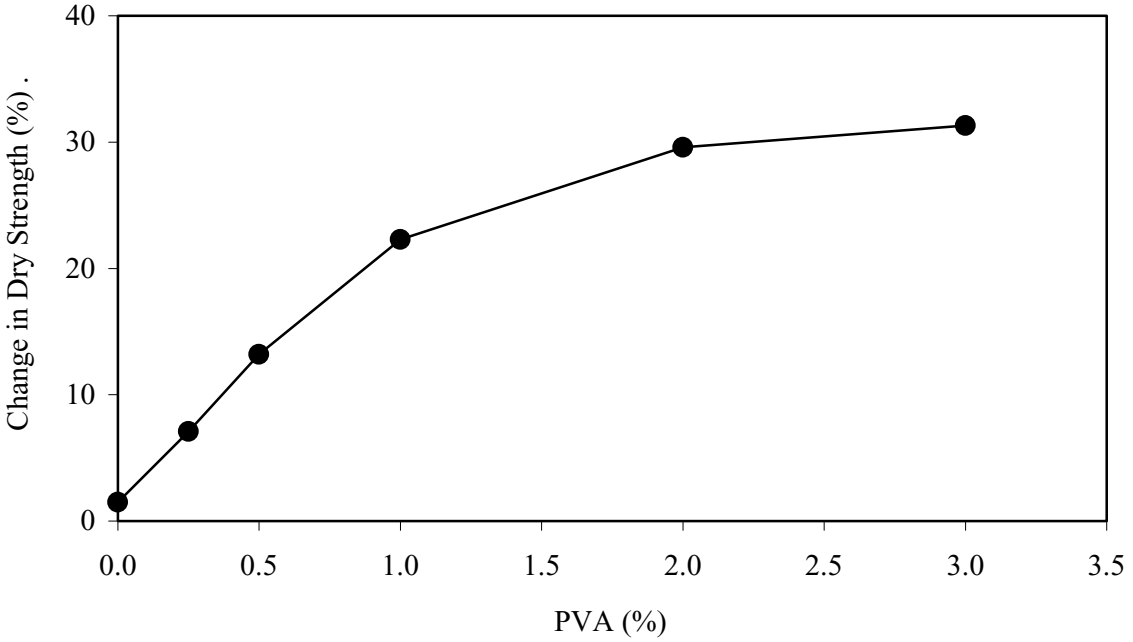

Figure 6.6. Dry strength of paper treated with 2.0% glutaraldehyde combining different amounts of PVA, cured at 130^{o}C

Figures 6.6 displays the dry strength of kraft paper treated with 2.0% glutaraldehyde in combination with different amounts of PVA and cured at 130^{o}C for 1.5 min. One observes that the addition of PVA imparts striking increase in dry strength for paper crosslinked by glutaraldehyde. The dry strength increases rapidly when the PVA concentration increases, particularly at concentration level lower than 1.0%.

The effect of crosslinking on the dry properties of paper can be attributed to the nature of crosslinks produced in the fiber network. Due to small molecular size, glutaraldehyde is able to penetrate into fibers and to produce short linkages between cellulosic molecules inside of the fibers [17]. Even though some glutaraldehyde also produced crosslinks between fibers in fiber crossing areas, the crosslinks are located predominantly in the amorphous regions of fiber wall. The intrafiber crosslinks restrict the mobility of microstructural units of fibers. This is the reason why glutaraldehyde is able to impart wrinkle resistance to cotton fabrics [17].

When PVA is used as a co-additive in the crosslinking system, glutaraldehyde may react with the hydroxyl groups of both PVA and cellulose through the formation of acetal links in the presence of the catalysts. PVA has approximate molecular weight of 80,000-170,000. A long PVA molecule is able to chain many glutaraldehyde molecules together (pentanedialated-PVA). If the ratio between PVA and glutaraldehyde is appropriately controlled, there can be numerous highly reactive aldehyde and hemiacetal groups left in the pentanedialated-PVA. Because of its bulky size, the molecules of PVA are not able to penetrate into fiber and tend to stay on fiber surface instead. Thus, the reaction between glutaraldehyde and cellulose and that between glutaraldehyde and PVA produce long-range crosslinks.

The short intrafiber crosslinks produced by glutaraldehyde do not contribute to fiber bonding and thus have little affect on the dry strength of paper. The slight increase in dry strength of glutaraldehyde-treated paper (Figure 6.1) results from the limited amount of interfiber crosslinks. However, both intrafiber and interfiber crosslinks produced by glutaraldehyde are short and stiff. They increase the rigidity of fibers and the fiber network, thus causing more heterogeneous distribution of stress in the paper network. The total result is the reduction in stretch of treated paper. As the amount of short crosslinks increases, the diminished extensibility leads to premature disruption of paper, thus reduces the dry strength. This is an important reason why paper treated with high level of glutaraldehyde exhibits serious loss of dry strength.

The addition of PVA improves the dry performance of paper through two possible mechanisms. The interfiber crosslinks through cellulose-glutaraldehyde-PVA-glutaraldehyde-cellulose linkages reinforce the fiber bonding and thus increase the dry strength. When paper is wetted by a glutaraldehyde/PVA solution and then dried, PVA moves to fiber crossover areas and is driven into pores and cracks in fiber surface by the capillary force. The interfiber areas are the centers of stress transfer in the network, and the pores and cracks are the weak points of fiber. Thus, PVA strengthens the weak points of fibers and enhances the stress dissipation of network.

The concentrations and PVA/glutaraldehyde ratio need to be optimized to ensure maximum performance of treated paper. As shown in Figures 6.4 and 6.5, with addition of 1.0% PVA, dry strength and tensile energy absorption of treated paper reach the highest values at the 2.0% glutaraldehyde concentration level, then decrease as the glutaraldehyde concentration increases further. This phenomenon can be explained based

on the amount of free glutaraldehyde. PVA can only react with certain amount of glutaraldehyde, and excess amount of free glutaraldehyde has negative effects on dry strength and tensile energy absorption as explained previously.

Folding Endurance

Figure 6.7 shows the folding endurance of kraft paper treated with 2.0% glutaraldehyde with and without 1.0% PVA and cured at temperatures ranging from 110 to 140^{o}C for 1.5 min. The treatment with 2.0% glutaraldehyde reduces the folding endurance by 100-200 double folds. Addition of PVA significantly improves the folding endurance of the treated paper. The folding endurance increases drastically when PVA is added, particularly at low concentration levels up to 1.0% (Figure 6.8). Treatment with

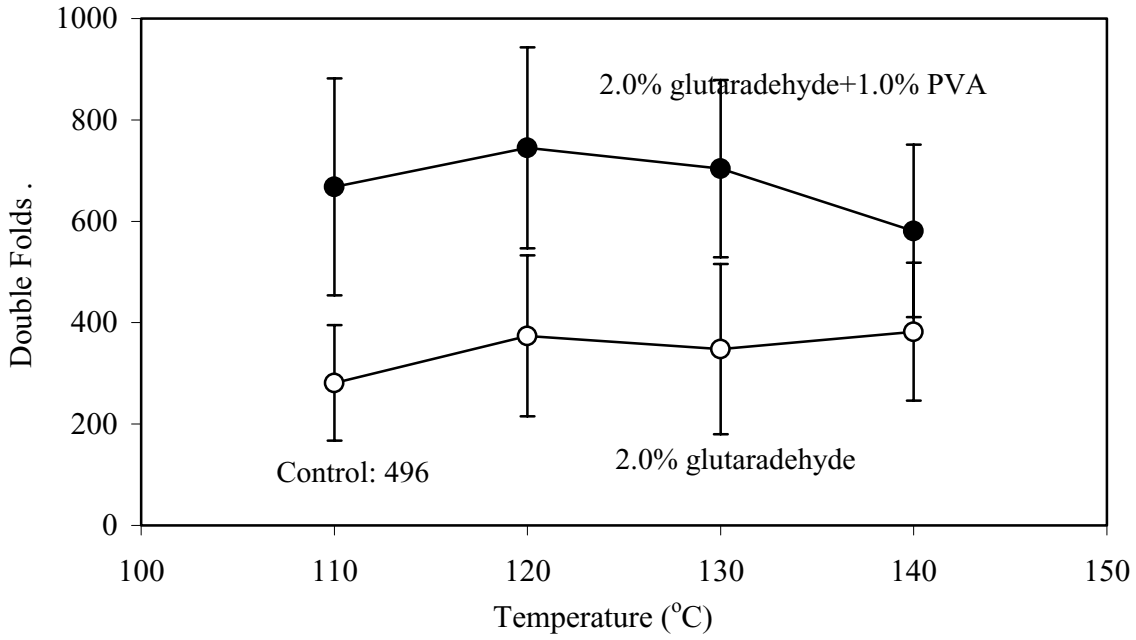

Figure 6.7. Folding endurance of paper treated with 2.0% glutaraldehyde with and without 1.0% PVA, cured at different temperatures. Error bars indicate the standard deviation of testing data

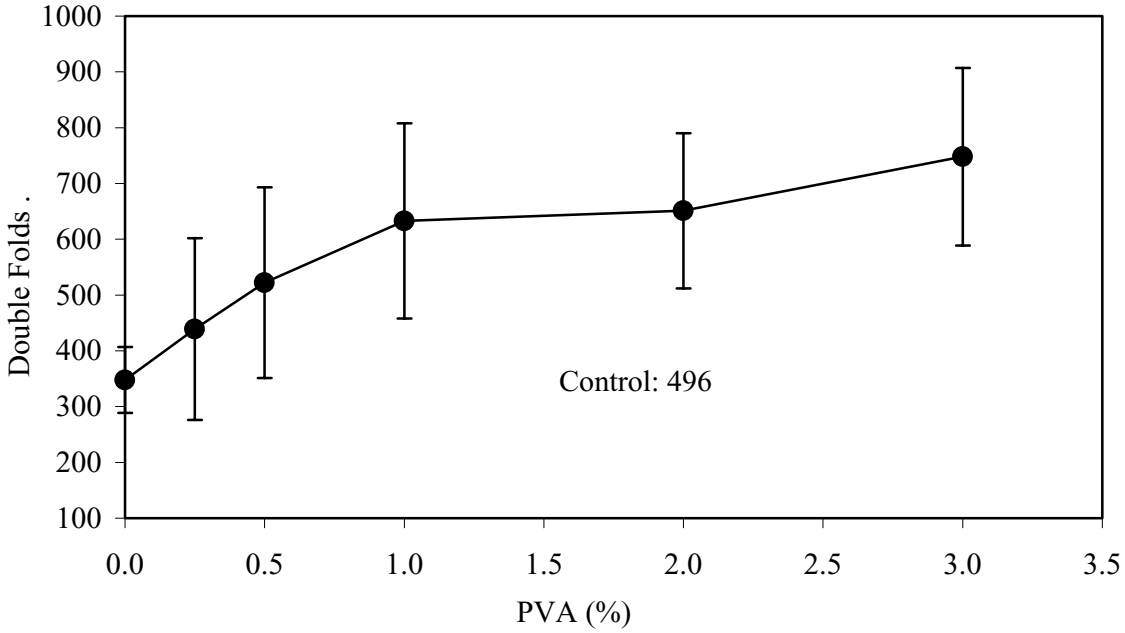

Figure 6.8. Folding endurance of paper treated with 2.0% glutaraldehyde combining different amounts of PVA, cured at 130^{o}C. Error bars indicate the standard deviation of testing data.

the combination of 2.0% glutaraldehyde and 1.0% PVA leads to an increase of 140 double folds over that of the control sample, even though the control sample has excellent folding endurance.

Folding endurance is a sensitive property associated with flexibility or flow property of paper [18]. During the folding test, the fiber-fiber bonds are loosening gradually, which leads to decrease in tensile strength and final fracture of paper. Mason [19] believes that high folding endurance is obtained when the papers have a high rate of stress relaxation and relatively primary creep. The paper treated by glutaraldehyde suffers from reduction in folding endurance due to embrittlement. PVA reduces the amount of free glutaraldehyde and produce crosslinks between fibers. The polymer in the fiber crossing area improves the efficiency of stress relaxation in the fiber network.

Wet Strength

Figure 6.9 displays the wet strength of kraft paper treated with 2.0% glutaraldehyde and the combination of 2.0% glutaraldehyde and 1.0% PVA and cured at temperatures ranging from 110 to 140^{o}C for 1.5 min. Because the dry strength changes as a result of the treatment, we use the ratio of wet strength of treated paper to the dry strength of control sample (W/D) as the basis to evaluate the improvement in wet strength. The data show that wet strength of the paper treated by glutaraldehyde with and without 1.0% PVA increases as curing temperature increases. One finds that addition of 1.0% PVA provides nearly 10% increase in wet strength for the paper treated with 2.0% glutaraldehyde.

The wet strengths of kraft paper treated with the combination of 1.0% PVA and glutaraldehyde of different concentrations and cured at 130^{o}C for 1.5 min are shown in

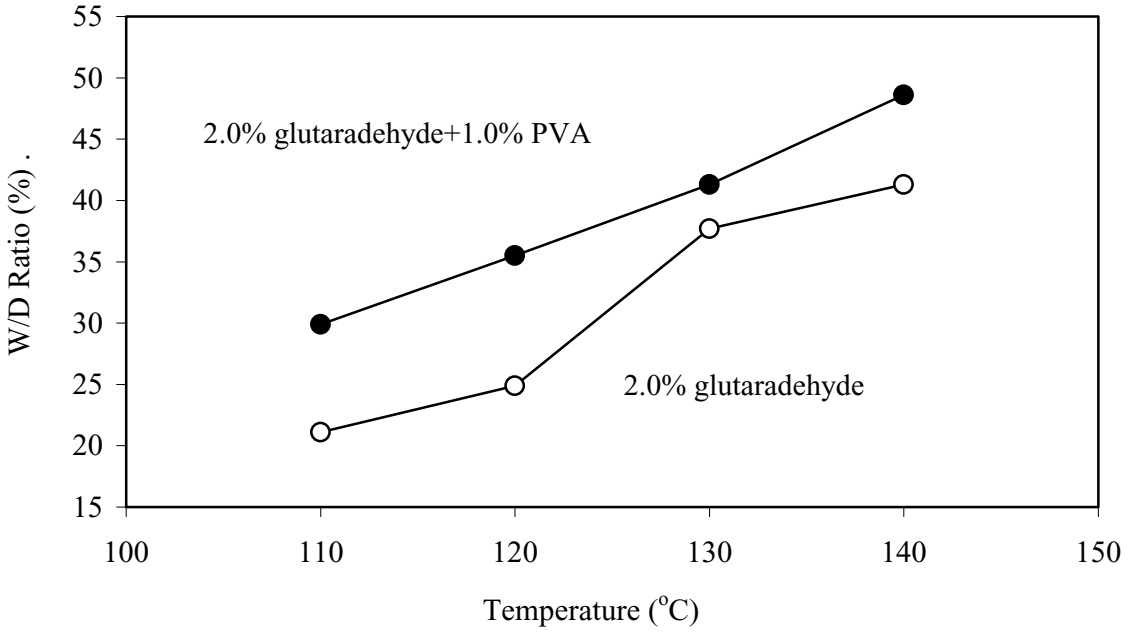

Figure 6.9. Wet strength of paper treated with 2.0% glutaraldehyde with and without 1.0% PVA, cured at different temperatures

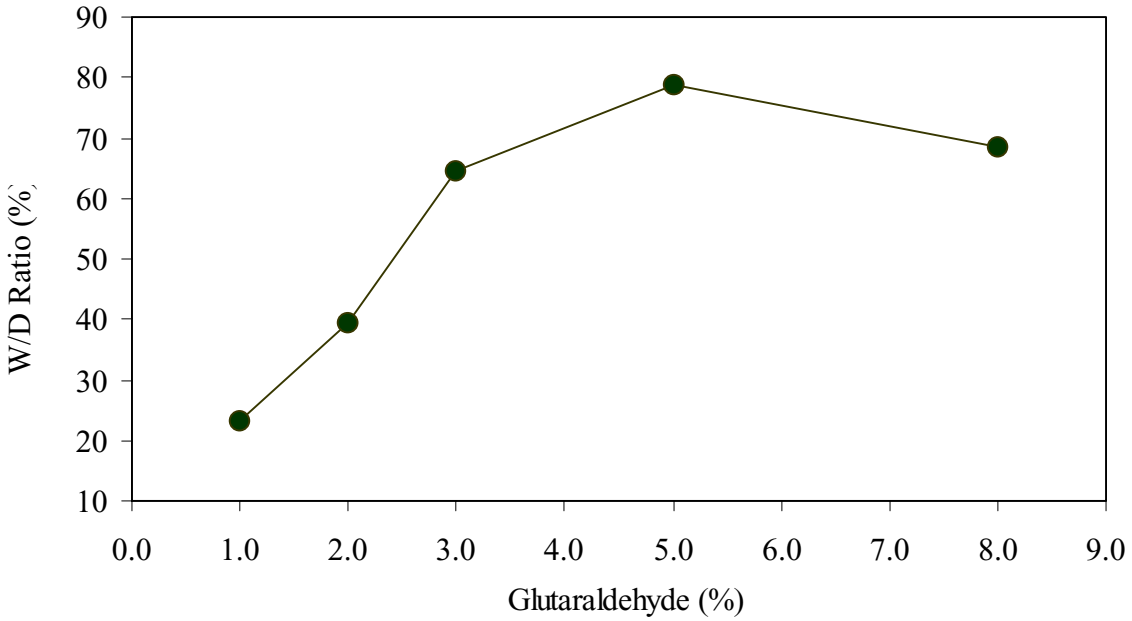

Figure 6.10. Wet strength of paper treated with different amounts of glutaraldehyde combining 1.0% PVA, cured at 130^{o}C

Figure 6.10. One observes that wet strength of the treated paper increases proportionally to the concentration of glutaraldehyde up to 5.0%.

It is a fact that the addition of PVA to glutaraldehyde reduces amount of reactive aldehyde and hemiacetal groups available to react with cellulose. Yet 2.0% glutaraldehyde in combination with 1.0% PVA is still able to produce higher wet strength than 2.0% glutaraldehyde alone.

There are two possible reasons for the improvement of paper wet strength by the addition of PVA. The crosslinking network in the paper produced by glutaraldehyde and PVA is more efficient in shielding the interfiber hydrogen bonds from disruption by water when the paper is exposed to wet environment. Secondly, addition of PVA increases dry strength of paper as discussed previously. Based on the preservation

mechanism of wet strength retention, the paper with stronger dry strength will retain higher wet strength.

CONCLUSION

The crosslinking system, i.e., glutaraldehyde/PVA/catalyst, possesses high efficiency for improving wet strength, dry strength, and folding endurance of paper. The combination of PVA as a co-additive not only improves wet strength but also brings about significant improvement in dry strength, stretch, tensile energy absorption, and folding endurance of the paper crosslinked by glutaraldehyde. A probable explanation for the excellent performance of the crosslinking system is the formation of interfiber crosslinking network through the reaction of glutaraldehyde to both PVA and cellulose. Compared to the short crosslinkages produced by glutaraldehyde, the crosslinking network formed by glutaraldehyde and PVA not only show higher efficiency in improving wet strength but also contributes to the improvement in dry performance of the treated paper.

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CHAPTER 7

FURTHER INVESTIGATION ON DIALDEHYDES AND POLY(VINYL ALCOHOL) FOR IMPROVING PAPER WET STRENGTH[1]

[1]Xu, G.G. and C.Q. Yang. 2001. To be submitted to Journal of Pulp and Paper Science.

ABSTRACT

Glutaraldehyde and glyoxal in combination with fully hydrolyzed poly(vinyl alcohol) (PVA) are investigated to improve wet strength of kraft paper. The properties of the paper crosslinked by the two dialdehydes alone and by the combination of a dialdehyde and PVA are compared. Dialdehydes alone improve wet strength of paper at the expense of dry strength and folding endurance. Combining PVA as a co-additive with dialdehydes not only significantly improves the wet strength but also increases dry strength and folding endurance of treated paper. Glutaraldehyde is able to impart much higher wet strength and better dry strength and folding endurance to treated paper than glyoxal. The wet strength of glutaraldehyde-treated paper not only increases linearly with the additional amount of PVA, but also increased with the molecular weight of PVA. Different catalysts, including $Zn(NO_3)_2$, $AlCl_3$, NH_4Cl , $MgCl_2$, are investigated to promote the crosslinking acetalization. It is found that NH_4Cl, and particularly $Zn(NO_3)_2$, are effective for acidic and neutral conditions.

INTRODUCTION

Continuous effort has been made to develop novel wet strength resins of paper without emission of formaldehyde and adsorbable organic chlorides (AOX) [1-11]. Ester crosslinking of cellulose using 1,2,3,4-butanetetracarboxylic acids (BTCA) and poly(maleic acid) (PMA) improves wet strength of paper with deteriorated dry strength and folding endurance [1-6]. There have been two approaches to minimizing the paper embrittlement caused by esterification crosslinking with polycarboxylic acids of small size [7, 8, 9]. The first approach is using high molecular weight maleic anhydride copolymers instead of small molecular weight polycarboxylic acid [7, 8]. Poly(ethene-co-maleic anhydride) [7] and poly(methyl vinyl ether-co-maleic anhydride) [8] not only exhibited higher efficiency for improving wet strength but also significantly improved the dry strength and folding endurance of treated paper. The second approach is adding small amount of high molecular weight poly(vinyl alcohol) (PVA) as co-additive [9]. PVA improved the dry strength and folding endurance of paper treated with poly(maleic acid). One disadvantage of the esterification crosslinking is the necessity to use curing temperature as high as 170^{o}C for efficient reaction.

In order to reduce the curing temperature, we evaluated dialdehydes as wet strength agents of paper [10]. It was found that glutaraldehyde is very effective in improving durable wet strength of paper at relatively lower curing temperatures (around 120^{o}C). Similar to polycarboxylic acids of small molecular sizes, glutaraldehyde also caused paper embrittlement. Adding PVA as co-additive also significantly improved the dry strength and folding endurance of treated paper [11]. The objective of this study is to further improve the performance of dialdehyde/PVA as wet strength resin for paper products by optimizing selection of catalyst, pH, and PVA.

EXPERIMENTAL

Materials

The paper used in this research was unbleached kraft paper with grammage of 65g/m^2. Glyoxal was a 40% aqueous solution. Glutaraldehyde was a 50% aqueous solution. A fully hydrolyzed poly(vinyl alcohol) PVA with a viscosity of 62-72 cps (PVA) was used for most of treating solutions in the study. Another fully hydrolyzed PVA with a lower viscosity of 28-32 cps (PVA-1) was to investigate the effect of molecular weight of PVA to the wet and dry strength of treated paper. $Zn(NO_3)_2$, $AlCl_3$, NH_4Cl, $MgCl_2$ were all regent grade chemicals. All treating solutions contained either 1.16% glyoxal (0.20M) or 2.0% glutaraldehyde (0.2M) in combination of different amounts of poly(vinyl alcohol). 0.758% $Zn(NO_3)_2$, or 0.53% $AlCl_3$, or 0.38% $MgCl_2$ (the three metal salts in same mole concentration), or 0.53% NH_4Cl, was used as catalyst according to need. Citric acid and NaOH were used to adjust pH of the treating solution.

Paper Treatment

The kraft paper sheets with a size of 25x25 cm^2 were immersed in a solution for 30 seconds, then pressed between squeezing rolls to remove the excess liquid and to reach about 95% wet pick-up. The impregnated sheets were dried on a hot plate dryer at 85^oC for 3 min to prevent curling. Each sheet was cured in a force draft oven at specified temperatures for 1.5 min. The cured sheets were rinsed in running water for 15 minutes to remove unreacted chemicals, and then dried. The control sample was treated with pure water and cured at 130^oC. Five specimens were treated under each condition.

Paper Performance Testing

Dry tensile strength, wet tensile strength, and folding endurance of the treated paper sheets were evaluated according to TAPPI standard test methods T 494 om-96, T456 om-87, and T 511 om-96, respectively. For wet tensile strength, the specimens were immersed in distilled water for 10 min, 0.5 hour, or 24 hours before testing. Ten measurements were performed for each testing procedure.

The wet strength (W/D ratio) was expressed as ratio of wet strength of treated paper to the dry strength of control sample. The dry strength was expressed as percentage changes over that of control sample.

RESULTS AND DISCUSSION

Wet Strength

The catalyst is important for the crosslinking resins to improve wet strength of paper. Figure 7.1 shows the wet strength of paper treated with 2.0% (0.20 mol/L) glutaraldehyde and 1.173% PVA without use of catalyst and cured at different temperatures. The wet strength of paper was tested after soaking in water for 10 min, 0.5 hour, and 24 hours. The control sample had a W/D of 10-12% after soaking for 10 min and 24 hours. The data indicate that glutaraldehyde/PVA only provides slightly improvement in the wet strength of paper when no catalyst is used. Figure 7.2 presents the wet strength of paper treated with 1.16% (0.20 mol/L) glyoxal and 1.173% PVA with no catalyst and cured at different temperatures. On observes that the curing temperatures did not significantly affect the wet strength of treated paper, similar to the treatment with glyoxal without a catalyst [10]. All treated paper samples showed an initial W/D ratio between 40% to 46%, which decreased to 30-33% after 0.5 hour of

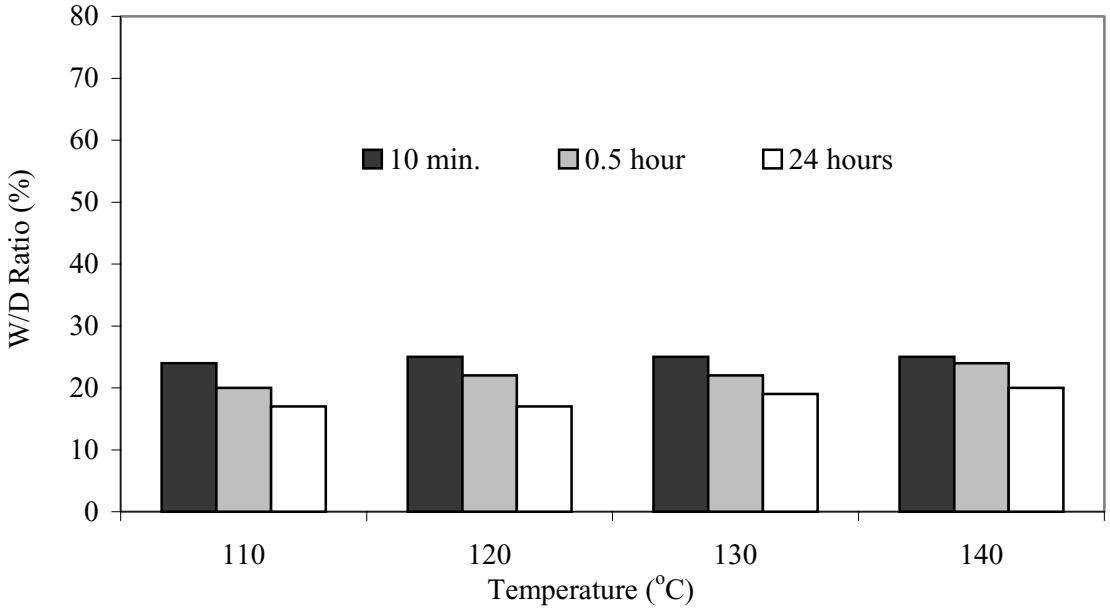

Figure 7.1. Wet strength after being soaked in water for 10 min, 0.5 hour, and 24 hours, paper treated with 2.0% (0.20 mol/L) glutaraldehyde and 1.173% PVA without a catalyst, pH 4.3, cured at different temperatures

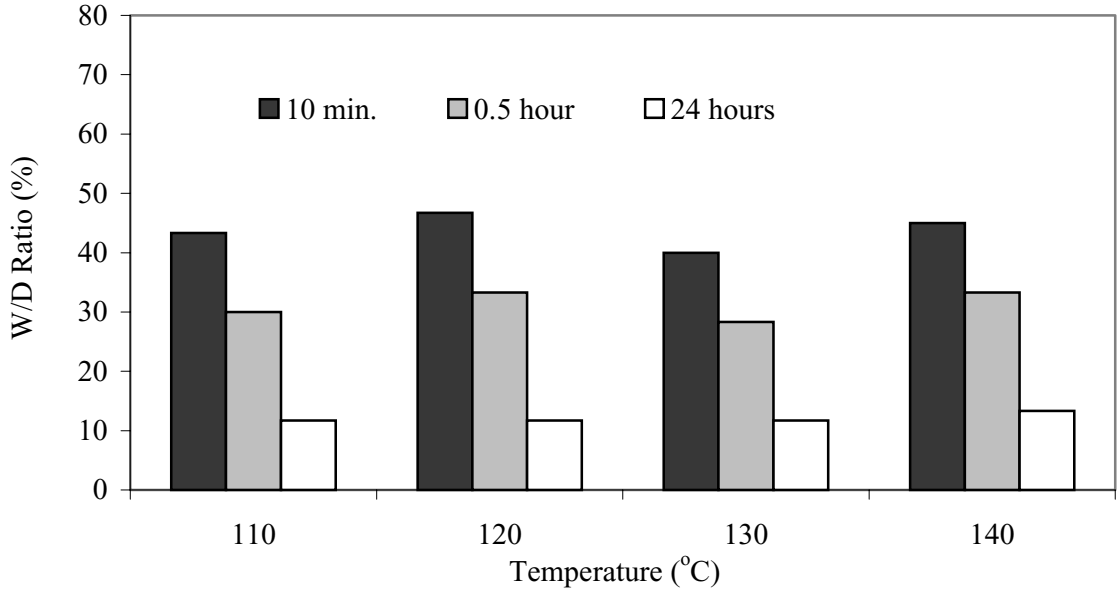

Figure 7.2. Wet strength after being soaked in water for 10 min, 0.5 hour, and 24 hours, paper treated with 1.16% (0.20 mol/L) glyoxal and 1.173% PVA without a catalyst, pH 4.3, cured at different temperatures

soaking, and 12-14% after 24 hours of soaking in water. It suggests that the glyoxal/PVA-treatment without a catalyst imparts only temporary wet strength to the paper. It is common knowledge that aldehyde reacts with hydroxyl groups to form semi-acetal [12], which is easily hydrolyzed in water. The aldehyde groups are more electronic deficient thus more reactive in glyoxal than in glutaraldehyde. Therefore, glyoxal is able to react with hydroxyl in poly(vinyl alcohol) and cellulose readily and form semi-acetal crosslinks on cellulose fibers thus provide temporary wet strength, while glutaraldehyde is less reactive than glyoxal and provides lower temporary wet strength.

The wet strength of the paper treated with 1.16% (0.20 mol/L) glyoxal and 1.173% PVA with addition of 0.758% $Zn(NO_3)_2$ as a catalyst and cured at different temperatures is presented in Figure 7.3. The initial wet strength (after being soaked in water for 10 min) of the treated paper is similar to that in Figure 7.2. The wet strength after being soaked for 0.5 hour and 24 hours, however, increased gradually as curing temperature was raised. The W/D ratio after 24 hours' soaking increased from 20% at 110^{o}C to 35% at 150^{o}C. It means that the wet strength becomes more durable to hydrolysis at higher curing temperatures.

The wet strength of kraft paper treated by 2.0% (0.20mol/L) glutaraldehyde and 1.173% PVA with addition of 0.758% $Zn(NO_3)_2$ as a catalyst and cured at different temperatures is illustrated in Figure 7.4. Two major differences are found between glyoxal (Figure 7.3) and glutaraldehyde (Figure 7.4). Firstly, glutaraldehyde/PVA imparted much high levels of durable wet strength than glyoxal/PVA at all curing conditions. For the glutaraldehyde-treated paper, its W/D ratios remained almost unchanged during 24-hours' soaking in water. Secondly, glutaraldehyde/PVA showed

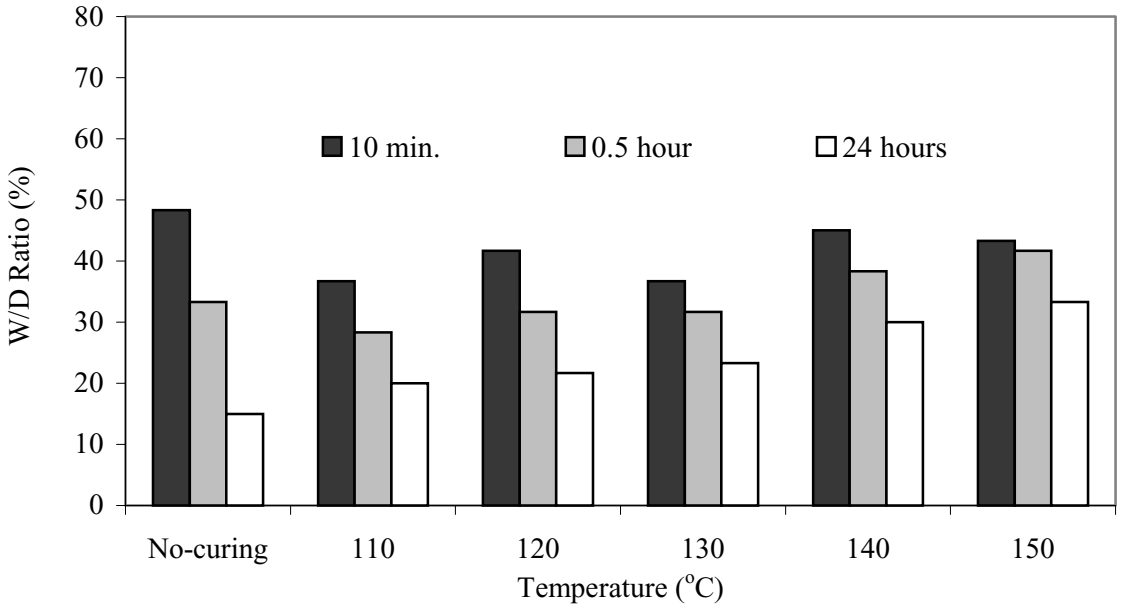

Figure 7.3. Wet strength after being soaked in water for 10 min, 0.5 hour, and 24 hours, paper treated with 1.16% (0.20 mol/L) glyoxal, 1.173% PVA, and 0.758% $Zn(NO_3)_2$, pH 4.3, cured at different temperatures

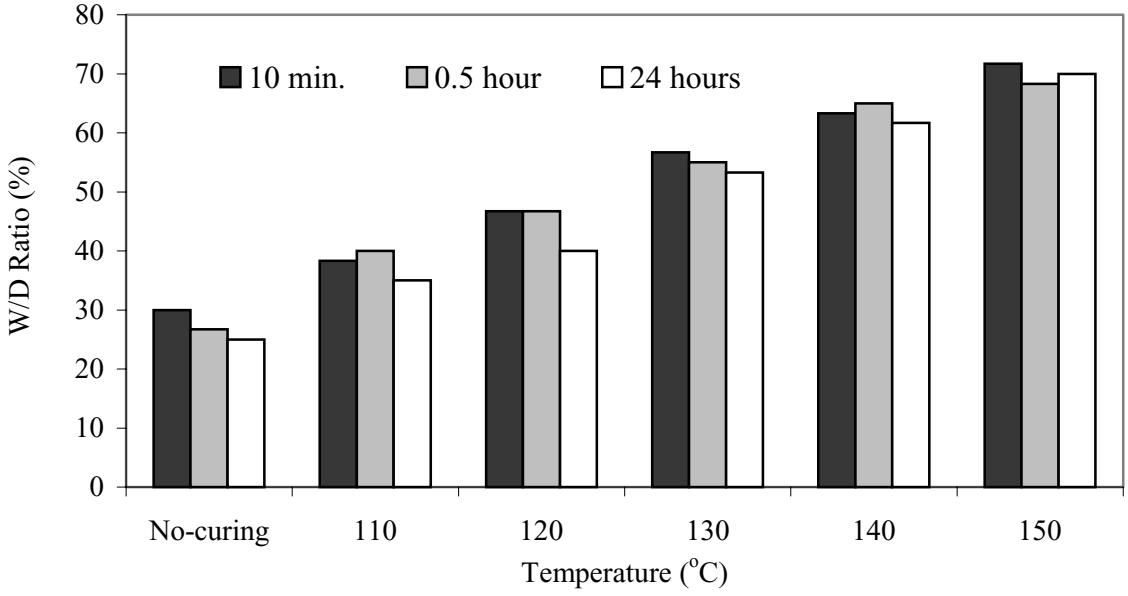

Figure 7.4. Wet strength after being soaked in water for 10 min, 0.5 hour, and 24 hours, paper treated with 2.0% (0.20 mol/L) glutaraldehyde, 1.173% PVA, and 0.758% $Zn(NO_3)_2$, pH 4.3, cured at different temperatures

much higher effectiveness than glyoxal/PVA for improving durable wet strength of paper. The W/D ratio after being soaked for 24 hours increased from 35% at 110^{o}C to 70% at 150^{o}C (Figure 7.4), which are much greater in magnitude than those of glyoxal-treated paper as shown in Figure 7.3.

The durability of wet strength is attributed to the formation of acetal instead of hemiacetal cross-links. Aldehyde reacts with hydroxyl group to form hemiacetal, but the reaction will proceed further to form acetal under the catalysis of a Lewis acids [12]. Hemiacetal is easily hydrolyzed by water, in contrast, acetal is stable under neutral and alkaline conditions. As a consequence, hemiacetal crosslinks result in only temporary wet strength, while acetal crosslinks impart durable wet strength to paper. High curing temperature increases acetalization rate and shifts the reaction equilibrium to the direction of acetal formation [12].

The distinct effectiveness of glyoxal and glutaraldehyde is possible a result of their different steric structure thus reactivity for acetalization. For glyoxal, the two aldehyde groups are too close to each other, making them difficult to react with four hydroxyl groups in cellulose or poly(vinyl alcohol) simultaneously to create two acetal crosslinks on the fibers.

The effect of different catalysts on the performance of treated paper was also investigated. The paper was treated with 2.0% glutaraldehyde, 1.173% PVA, and different salts of same mole concentration (except NH_4Cl) at different pH conditions, and cured at 130^{o}C for 1.5 min. The wet strength (after being soaked for 24 hours) of the treated paper was tested and shown in Figure 7.5. One finds that the wet strength of paper treated with $AlCl_3$ and $MgCl_2$ as catalysts decreased quickly when pH is higher than 4.0.

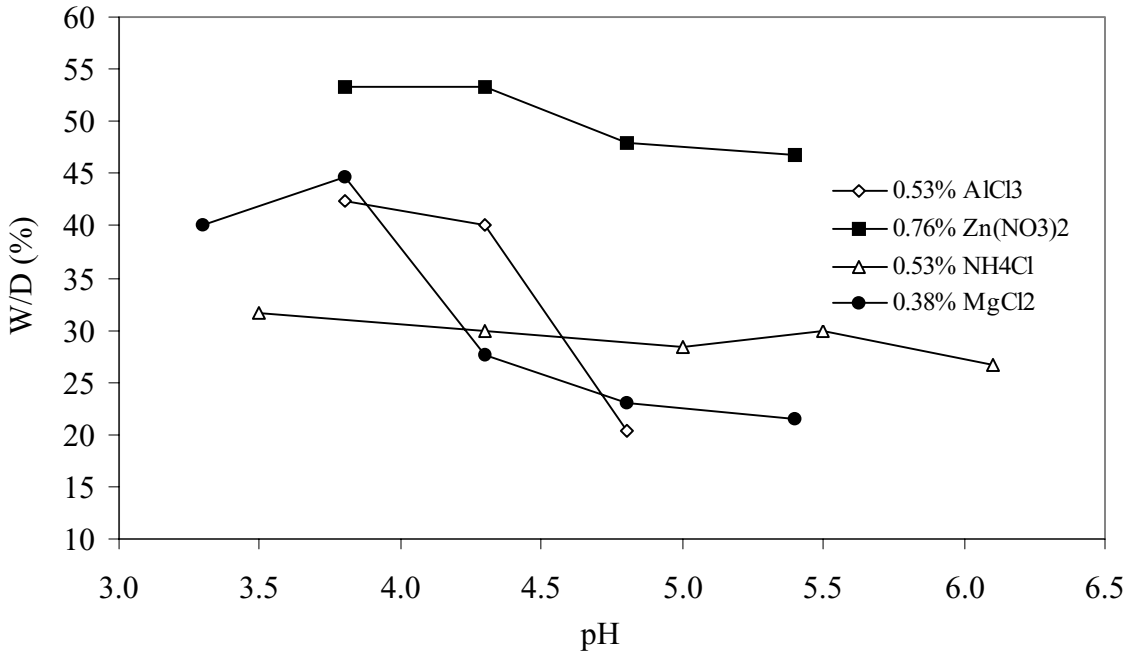

Figure 7.5. Wet strength (24 hours' soaking) of the paper treated with 2.0% glutaraldehyde, 1.173% PVA, and different catalysts at various pH, cured at 130^{o}C

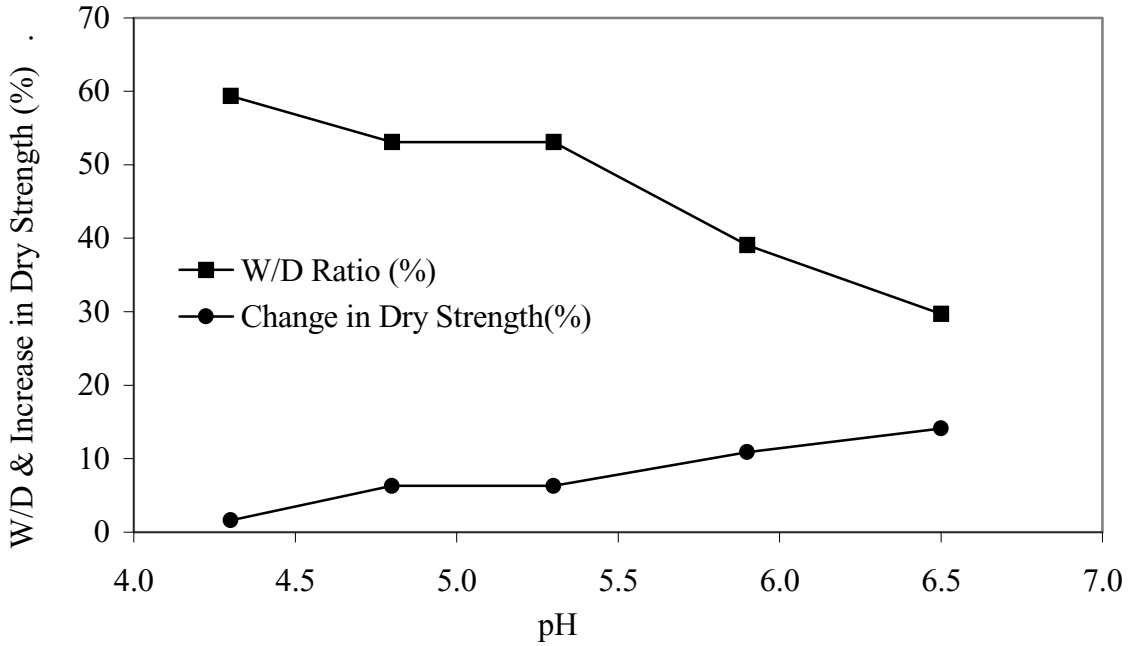

Figure 7.6. Wet strength (24 hours' soaking) and dry strength of the paper treated with 2.0% glutaraldehyde,1.0% PVA, and 0.758% $Zn(NO_3)_2$, at various pH, cured at 140^{o}C

Meanwhile, NH_4Cl provided a relatively constant W/D ratio around 30-35% in wide pH range from 3.5 to 6.2, while $Zn(NO_3)_2$ remained high highly effective at pH up to 5.4 and provided a W/D ratio above 45%. This result suggests that $Zn(NO_3)_2$ is the best catalyst for the acetalization. Figure 7.6 shows the wet and dry strength of paper treated with 2.0% glutaraldehyde, 1.0% PVA, and 0.758% $Zn(NO_3)_2$ at a wide pH range and cured at 140^{o}C for 1.5 min. The W/D ratio of treated paper decreased from 60% at pH 4.3 to 30% at pH 6.5. As to the current preference of alkaline and neutral papermaking, $Zn(NO_3)_2$ and NH_4Cl would be the good choices as catalysts for the glutaraldehyde/PVA crosslinking resin.

The wet and dry strength of paper treated with 2.0% glutaraldehyde, 0.758% $Zn(NO_3)_2$, and different amounts of PVA are illustrated in Figure 7.7. The W/D ratio increases from 52% with no addition of PVA to 72% with addition of 3.0% PVA. The result suggests that PVA must have played an important role the crosslinking of cellulose by glutaraldehyde.

The role PVA plays in the crosslinking acetalization is also shown from the effect of its molecular weight to the wet strength of treated paper. The paper was treated with 2.0% glutaraldehyde and 0.758% $Zn(NO_3)_2$, with no addition of PVA, and addition of 1.0% PVA of different molecular weight. PVA had a viscosity of 62-72 cps, while PVA-1 had a viscosity of 28-32 cps. The wet strength after being soaked in water for 24 hours is presented in Figure 7.8. At all curing temperatures, addition of lower molecular weight PVA-1 and higher molecular weight PVA brought about 3.0-4.0% and 7.0-10% higher W/D to paper crosslinked by glutaraldehyde, respectively. Apparently, poly(vinyl alcohol) of higher molecular weight improves the wet strength of paper more efficiently.

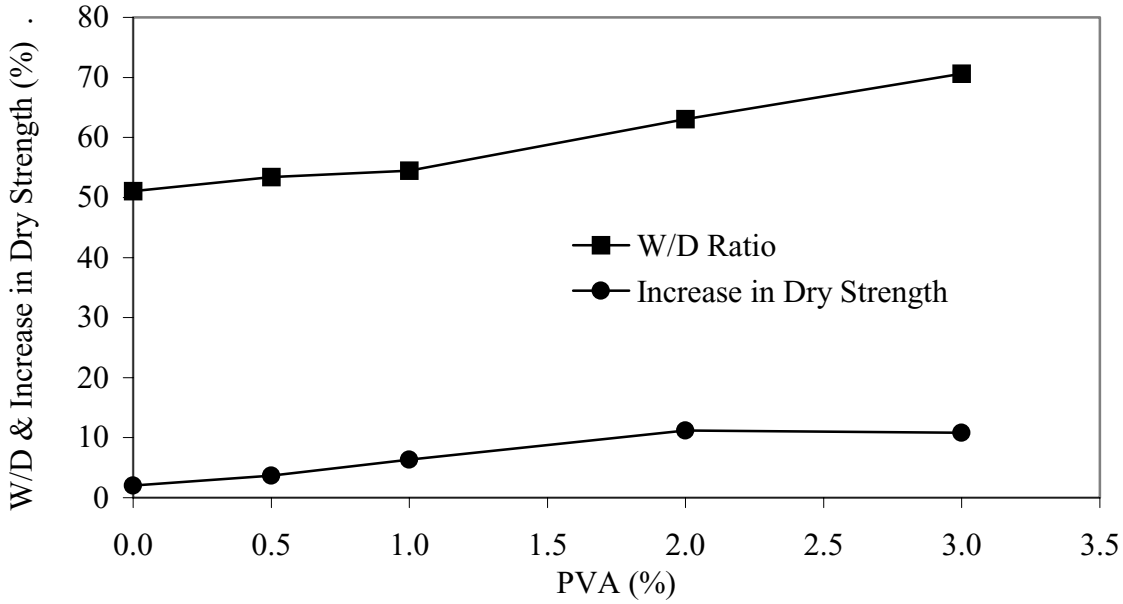

Figure 7.7. Wet strength (24 hours' soaking) and dry strength of the paper treated with 2.0% glutaraldehyde, 0.758% $Zn(NO_3)_2$, and different amounts of PVA, pH 5.3, cured at 140°C

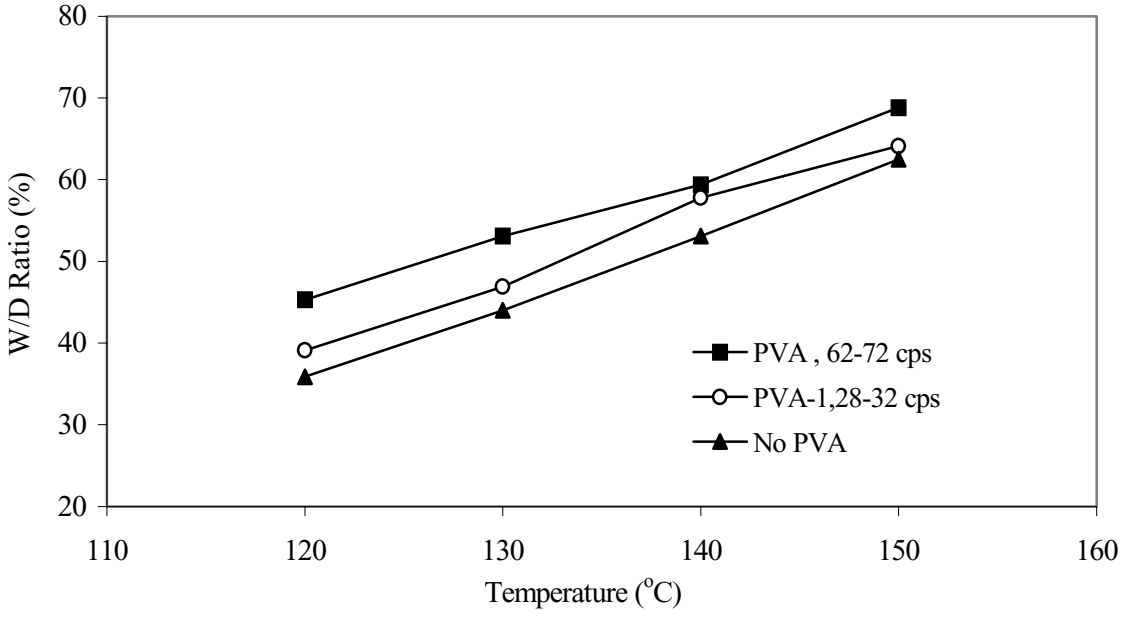

Figure 7.8. Wet strength (24 hours' soaking) of the paper treated with 2.0% glutaraldehyde, 0.758% $Zn(NO_3)_2$, without addition of PVA and addition of 1.0% PVA of different molecular weights, pH 4.3, cured at various temperatures

Dry Strength and Folding Endurance

The major concern about the wet strength improvement by BTCA, PMA, glutaraldehyde, and other reactive chemicals of small molecular size is the accompanying deterioration of dry strength and folding endurance of the treated paper. They improve the wet strength of paper at the cost of dry strength and folding endurance.

The relationship of folding endurance with wet strength of paper with different treatments is compared in Figure 7.9. The paper was treated with 1.16% (0.20M) glyoxal, 1.16% glyoxal/1.173% PVA, 2.0% (0.20M) glutaraldehyde, 2.0% glutaraldehyde/1.173% PVA and cured at 110, 120, 130, and 140^{o}C for 1.5 min. 0.758% $Zn(NO_3)_2$ was used as a catalyst in all cases. Because the change of folding endurance usually goes in the opposite direction to that of wet strength, the folding endurance is expressed as function of W/D ratio after being soaked in water for 24 hours. In all cases, the wet strength of treated paper increased as curing temperature was raised. For paper crosslinked with 2.0% glutaraldehyde, addition of 1.173% PVA not only provided a W/D ratio more than 10% higher in magnitude under all curing conditions, but also improved more than 250 double folds for same W/D ratio. While for paper treated with 1.16% glyoxal, addition of 1.173% PVA also improved the W/D ratio for a magnitude of 5-10%, and folding endurance for about 100 double folds. Meanwhile, glutaraldehyde exhibited much higher efficiency for improving wet strength of paper and brought about much higher folding endurance to paper than glyoxal. Based on the same wet strength, the glutaraldehyde/PVA-treated paper exhibited a flexibility superior to that treated with glyoxal/PVA.

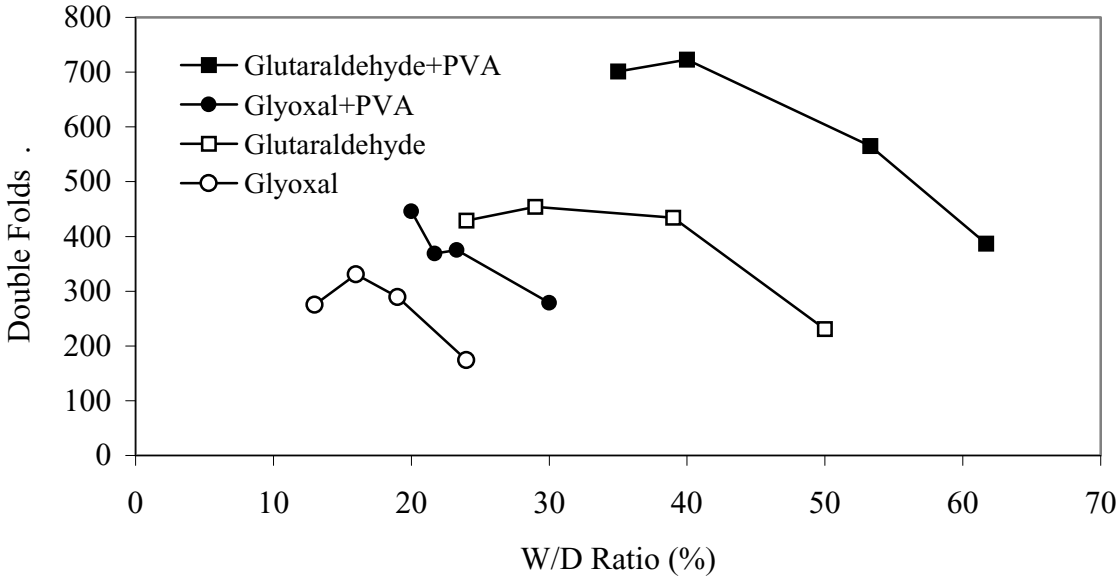

Figure 7.9. Folding endurance as a function of wet strength (24 hours' soaking), paper treated with 1.16% glyoxal, 1.16% glyoxal/1.173% PVA, 2.0% glutaraldehyde, and 2.0% glutaraldehyde/1.173% PVA, 0.758% $Zn(NO_3)_2$ used in all cases, pH 4.3, cured at 110, 120, 130, 140^{o}C

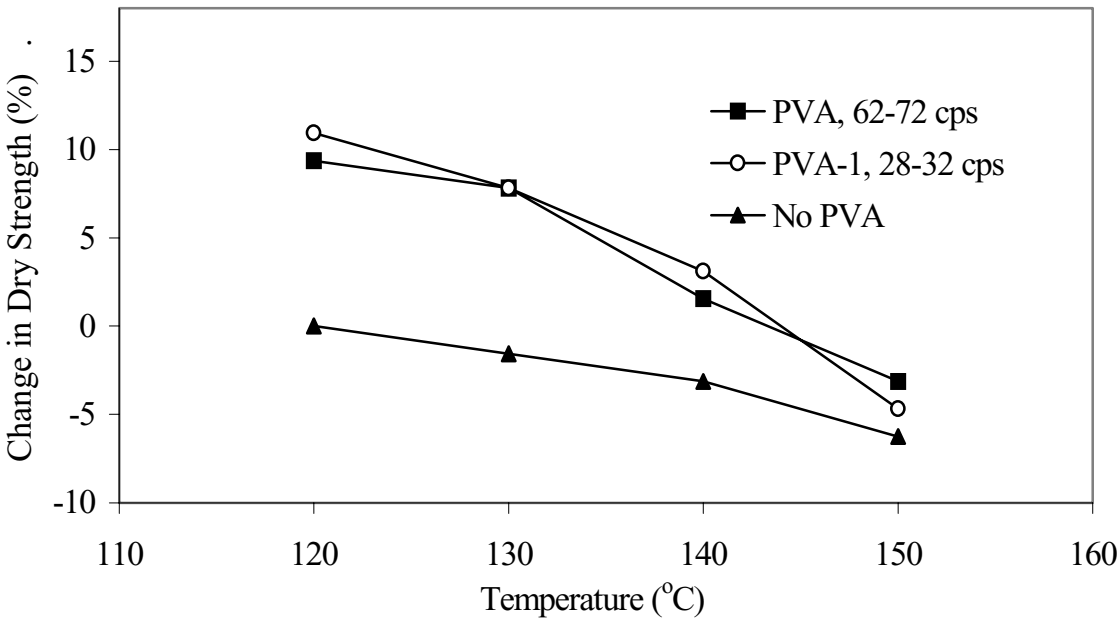

Figure 7.10. Dry strength of paper treated with 2.0% glutaraldehyde, 0.758% $Zn(NO_3)_2$, with no addition of PVA and addition of 1.0% PVA of different molecular weights, pH 4.3, cured at various temperatures

The change in dry strength of paper treated with 2.0% glutaraldehyde, 1.0% PVA, and 0.758% $Zn(NO_3)_2$ at different pH and cured at 140^oC for 1.5 min is shown in Figure 7.6. In contrast to wet strength, which decreased as pH was raised, the dry strength increased as pH increased. Dry strength increased for 2.0% at pH 4.3 and 15% at pH 6.5.

The increase in dry strength of paper treated with 2.0% glutaraldehyde, 0.758% $Zn(NO_3)_2$, and different amounts of PVA at pH 5.3 is present in Figure 7.7. The dry strength of paper increased with increasing addition of PVA up to 2.0%, while wet strength increased linearly with additional amount of PVA. The phenomenon is different from our previous study [11], where $MgCl_2$ was used as catalyst. The wet strength increased with increasing amount of PVA but leveled off at 1.0% of PVA, while dry strength increased fast as addition amount of PVA increased to 1.0% then slowly to 3.0%. The difference is possible due to the higher catalytic effectiveness of $Zn(NO_3)_2$ than that of $MgCl_2$. Over-crosslinking of cellulose leading to very high wet strength with a W/D ratio lager than 50%, may increase the heterogeneity of the cellulose fiber network thus reduce dry performance of treated paper.

Figure 7.10 compares the dry strength of paper treated with 2.0% glutaraldehyde and 0.758% $Zn(NO_3)_2$, with no addition of PVA, and addition of 1.0% PVA of different molecular weight. Treatment with glutaraldehyde alone affected inversely the dry strength. Including 1.0% PVA as co-additive brought about significant improvement in dry strength to treated paper particularly at low curing temperature. The two PVA of different viscosity did not show apparent difference for their contribution to dry strength.

CONCLUSION

The crosslinking system, i.e., glutaraldehyde/poly(vinyl alcohol)/catalyst, possesses very high efficiency for improving wet strength of paper. Glutaraldehyde is superior to glyoxal for improving durable wet strength without sacrificing dry performance of treated paper. Addition of PVA as a co-crosslinker not only significantly improves wet strength but also brings about striking increase in both dry strength and folding endurance of the paper crosslinked by dialdehydes. The wet strength of paper treated with glutaraldehyde increases not only with increasing additional amount of PVA but also with increasing molecular weight of PVA. It is believed that PVA participates in the crosslinking reaction of pulp cellulose with glutaraldehyde. $Zn(NO_3)_2$ is the most effective catalyst to promote the crosslinking acetalization of pulp cellulose by combination of glutaraldehyde and PVA. It remains highly effective in both acidic and neutral papermaking conditions.

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CHAPTER 8

THE MECHANISM OF WET STRENGTH OF PAPER IMPARTED BY POLYCARBOXYLIC ACIDS AND POLY(VINYL ALCOHOL)/GLUTARALDEHYDE[1]

[1]Xu, G.G. and C.Q. Yang. 2001. To be submitted to Journal of Pulp and Paper Science.

ABSTRACT

The mechanism of improving wet strength of paper by treating with poly(carboxylic acid)s and poly(vinyl alcohol)/glutaraldehyde was investigated by microscopic observation, liquid water swelling, water sorption, and Z-direction tensile strength. The Electron microscopic observation revealed that the paper crosslinked by high molecular weight poly(methyl vinyl ether-maleic acid) can be swollen by water to higher extent than that treated by low molecular weight poly(maleic acid), even though both had similar wet strength. High molecular weight polycarboxylic acid tends to stay on fiber surface and fiber crossing area, thus increases fiber contact area and produces interfiber crosslinking. Treatment of paper by glutaraldehyde alone improved wet strength and reduced swellability of paper due to intrafiber crosslinking. Combination of poly(vinyl alcohol) as co-cross-linker resulted in significantly increased wet strength, higher swellability, and improved fiber-fiber bonding. It is believed that poly(vinyl alcohol) reacts with glutaraldehyde and forms a bulky pentanedialated-PVA with little capacity to penetrate into fiber interior and results in inter-fiber crosslinking.

INTRODUCTION

It is well known that paper loses most of its strength when it is exposed to high humidity environment or soaked in water. The cause of weakening paper strength lies in the penetration of water into paper web and destruction of hydrogen bonds, which hold the cellulosic fibers together [1]. Crosslinking resins have been applied to improve the wet properties of paper [2]. However, the current wet strength resins are under scrutiny due to their emission of toxic formaldehyde or absorbable organic halides during production and use of paper products [3]. Therefore, there is need to develop alternatives to reduce the environmental impact by the paper wet strength resins.

Polymeric carboxylic acids have been investigated as environment-friendly wet strength agents of paper [3-12]. It is found that polymeric acids of small molecular size cause brittleness of paper and decrease the rupture energy and puncture resistance of treated paper, while the counterparts of high molecular weight do not sacrifice the flexibility of treated paper [10,11]. The different dry performance of paper crosslinked by polycarboxylic acids of low and high molecular weight possibly results from the different location of crosslinks induced by the polymeric acids.

Glutaraldehyde in combination with poly(vinyl alcohol) is also very efficient for improving wet strength of paper without sacrificing the dry performance of treated paper [13, 14, 15]. The resin possesses high efficiency at pH close to neutral condition and curing temperature as low as 110^{o}C for short curing time [15]. The wet strength of treated paper not only increases with additional amount of PVA but also increases with increasing molecular weight of PVA. It is important to understand the different behaviors of different resin and the nature of the resin-fiber interaction in the paper.

The improvement of wet strength of paper is accompanied with the change in its microstructure [16] and dimension stability. The dimensional stability is the property that paper swells or shrinks when exposed to environment of various humidity. The swelling of fibers in liquid water is much more significant than that in water vapor, and it brings about a stronger structure disorientation of cellulosic system [17]. The fiber transverse section increases to a much greater extent by water swelling than fiber length [18]. The ultimate water sorption and swelling depend not only upon the proportion of amorphous cellulose and its chemical composition present, but more upon the submicroscopic structure of fiber network [18]. It was reported that formaldehyde treatment of wood and cotton cellulose reduced the water sorption at 95% relative humidity to two thirds of that of control [19]. The cross-link restricts the internal accessibility of fibrous substrate, thus reducing the swelling of paper.

The swelling of fiber network can be visually studied by electron microscopy. Scanning electron microscopy (SEM) has become the most powerful tool to examine the surface topography of a variety of materials, because of its great depth of field and high resolving power [20]. The wet paper can be investigated directly by Cryo-SEM [21] and Environmental-SEM [22] or by normal SEM after critical point drying (CPD) [20]. CPD avoids intense surface tension during drying and maintains the fiber structure close to its wet state without severe collapse. In this study, the surface and cross section of wet paper after CPD, and the tensile fracture surface of dry paper were investigate using SEM.

The purpose of the study is to investigate the change in paper structure and water sorption induced by crosslinking of polymeric carboxylic acids and glutaraldehyde/PVA resins, and their relation with the wet and dry performance of treated paper.

EXPERIMENTAL

Materials and Methods for Electron Microscopic Examination

Paper and Treatment

The unbleached kraft paper were treated with 2.0% poly(maleic acid) (PMA) and poly(methyl vinyl ether-maleic anhydride) (PMMA) and cured at 170^{o}C for 1.5 min as described in previous paper [11]. PMA had a number average molecular weight (Mn) 800, while PMMA had a Mn of 1,130,000.

Swelling

The paper stripes of 1.5cm wide were brought into boil in a 50% aqueous methanol solution containing 0.5% wetting agent, cooled down and soaked overnight.

Critical Point Drying (CPD)

After exchanged by a series of aqueous ethanol solutions with ascending concentrations, 50%, 70%, 85%, 95%, 100%, the specimens were dried by critical point drying on a Samdri 780 Critical Point Dryer.

Coating

The paper stripes were cut into small pieces with a sharp razor. By using carbon tape, the specimens were mounted perpendicularly on aluminum stubs for observation of transverse section, while others mounted flatly for surface examination. The specimens were then coated with gold on a SPI Sputter Coater and stored in a desiccator before examined by SEM.

SEM Observation

The specimens were viewed and photographed with a JEOL JSM 5800 scanning electron microscope.

Materials and Methods for Water Retention and Dimensional Stability

Paper Treatment

The kraft paper was treated with 2.0% glutaraldehyde in combination of different amounts of fully hydrolyzed PVA with a viscosity 62-72 cps, and 0.758% of $Zn(NO_3)_2$ as catalyst as described in previous paper [15].

Tensile Strength Testing

Dry, wet, and Z-direction tensile strength of paper were evaluated according to TAPPI test methods T 494 om-96, T456 om-87, and T-541 om-99, respectively. For wet tensile strength, the specimens were soaked in water for 24 hours before testing. Ten measurements were performed for each testing procedure. The wet strength was expressed as a ratio of wet strength of treated sample to the dry strength of control sample (W/D ratio).

Water Retention

Water retention was measured by centrifuge method [23]. Small paper stripes about 0.5g, soaked in water for 24 hours, were placed in centrifuge tubes with perforated support. The sample was centrifuged at 3500 rpm for 6 min to remove the mechanically held water from the capillaries in the fiber network, then transferred to weighing bottles and weighed to get the wet weight W_w. The sample was then dried at 90^{o}C for 10 min, and weighed again to obtain the dry weight W_d . The water retention was determined according to the following formula: $WR\ (\%)=100\%\ (W_w-W_d)/W_d$

Thickness

The thickness of paper sheets was measured according to TAPPI test method T411 om-97. 20 measurements were performed for each sample.

RESULTS AND DISCUSSION

Microscopic Observation of Paper Crosslinked with Polycarboxylic Acids

Cross-section

The cross-sections of dry and CPD wet control sample are shown in Figure 8.1. Dry paper (Micrograph A) shows a dense cross-section with lumen disappeared almost completely, while the fibers are held together with some cavity between them. In contrast, the CPD wet paper (Micrograph B) has been swollen by water and fibers apparently separated. The CPD wet paper has a thickness double that of its dry counterpart, because the paper web was expanded by water between and inside fibers.

The cross-sections of paper treated by low molecular weight PMA is shown in Figure 8.2(A). It can be seen from the micrograph that few fibers were swollen. However, the space between fibers was expanded by water to some extent even though less than that of original paper. The reduction of fiber swelling suggests restriction of fibers by interior cross-links, while the separation between fibers indicates few cross-links exist between fibers. PMA oligomers are able to penetrate through pores into the fiber wall and produce predominately inter-lamella and inter-fibrilla cross-links but few inter-fiber crosslinks.

For paper treated by high molecular weight PMMA, the topographical feature of cross section its CPD wet sample is shown in Figure 8.2(B). The fibers exhibit significant fiber interior swelling but intimate contact between fibers. The fibers are swollen but strongly held together under the attack of water. Fiber interior swelling indicates few cross-links inside fibers, while close contact between fibers means strong inter-fiber bonding.

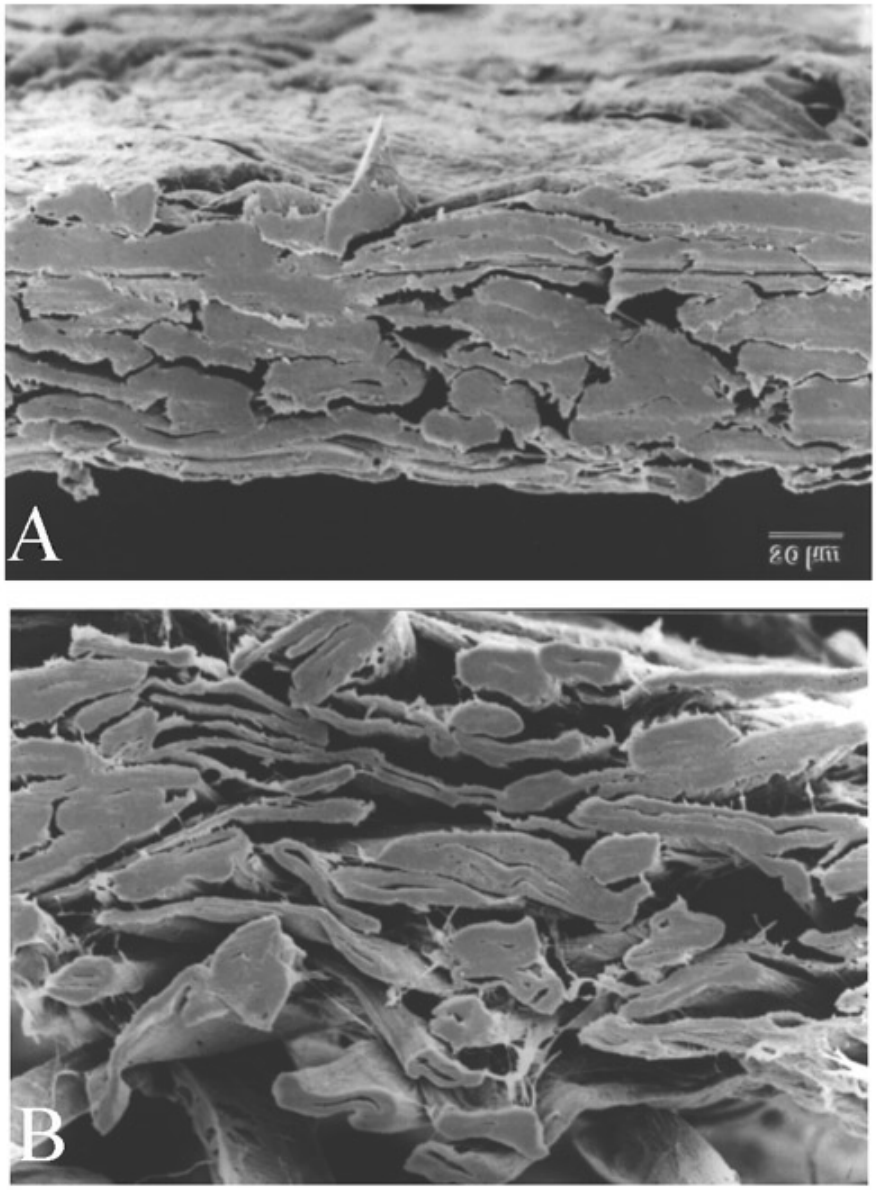


Figure 8.1 SEM micrographs of cross-section of control paper: A) dry; B) CPD wet

The swelling of the cellulosic network reflects the distribution of cross-links among the paper, which is dependent upon the accessibility of fibrous substrate to cross-linking agents. The accessibility of fiber interior and their response to physical and chemical

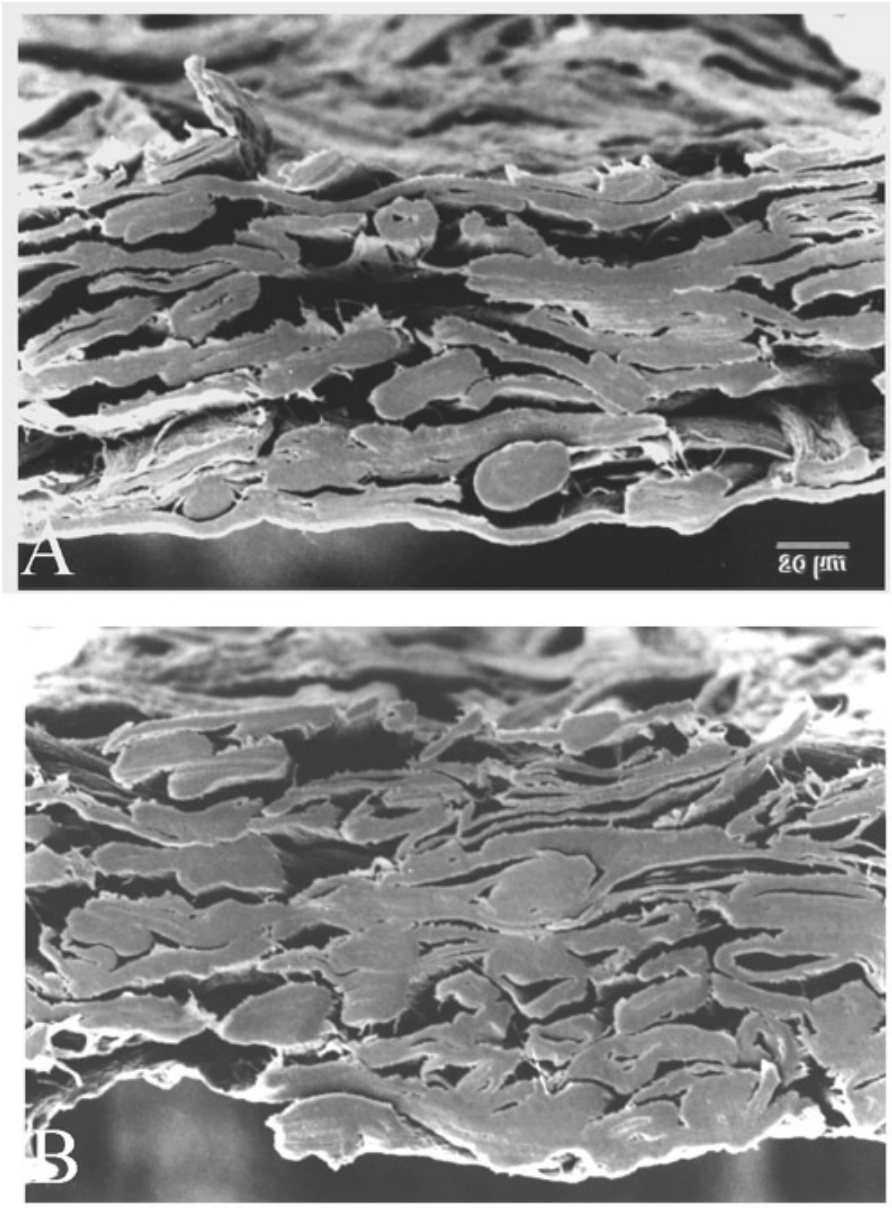


Figure 8.2 SEM micrographs of cross-section of CPD wet paper treated with 2.0% A) PMA and B) PMMA

interactions is dependent upon not only the number and size distribution of canulae, pores, interfibrillar interstices and cavities, but also the type and size of the reactant [18]. The molecular size of reactant in relation to the dimension of capillaries and fibrillar

interstices is decisively important for the course and extent of the chemical interaction. Small reactants are able to penetrate into the interstices between fibrillar aggregations, while larger reactants, such as reactive dye stuffs with a molecular size in the range of 3.0 to 4.5 nm, can only diffuse into fiber wall through larger pores and voids, such as those existing between lamellae of microfibrils (of about 100 to 150 nm lateral dimension) [18]. The Distribution of pore size on the cell wall depends upon the particular choice of wood species and pulping process. For unbleached kraft paper, the pore size distributes with a modal radius of about 1.0 μm, depending on the beating degree [24].

The dramatic difference of molecular size between PMA and PMMA results in extremely different depth of penetration and reaction in the fiber network. PMA with Mn of 800 has a mean extended molecular length around 1.5 nm and a random coil of dimension less than 1.0 nm, so it is able to diffuse freely into the fiber interior and produce inter-fibrillar and inter-lamellar cross-links. The intrafiber crosslinks restrict the accessibility and mobility of microstructure of fibers, leading to reduced swellability and increased brittleness of fibers. For PMMA with Mn of 1,130,000, because of its bulky size, it tends to stay on fiber surface or moves to crossover of fibers, thus increases fiber contact area and produces fiber-polymer-fiber bonds. The resin may also partly diffuse into fiber wall through large pores, leading to stronger resin-fiber anchoring. The increased fiber contact area and interfiber crosslinks reinforce and protect the fiber-fiber hydrogen bonds from disruption by water. Interfiber crosslinks improve dry strength but do not impose much impact on the swellability and internal mobility of fibers. Small water molecules are still able to penetrate freely into fiber interior and cause significant fiber expansion. Better internal mobility is related with higher folding endurance.

Surface

The surface of CPD wet paper samples treated with PMA and PMMA is shown in the Figure 8.3(A) and (B) respectively. A number of holes with sizes of microns found in

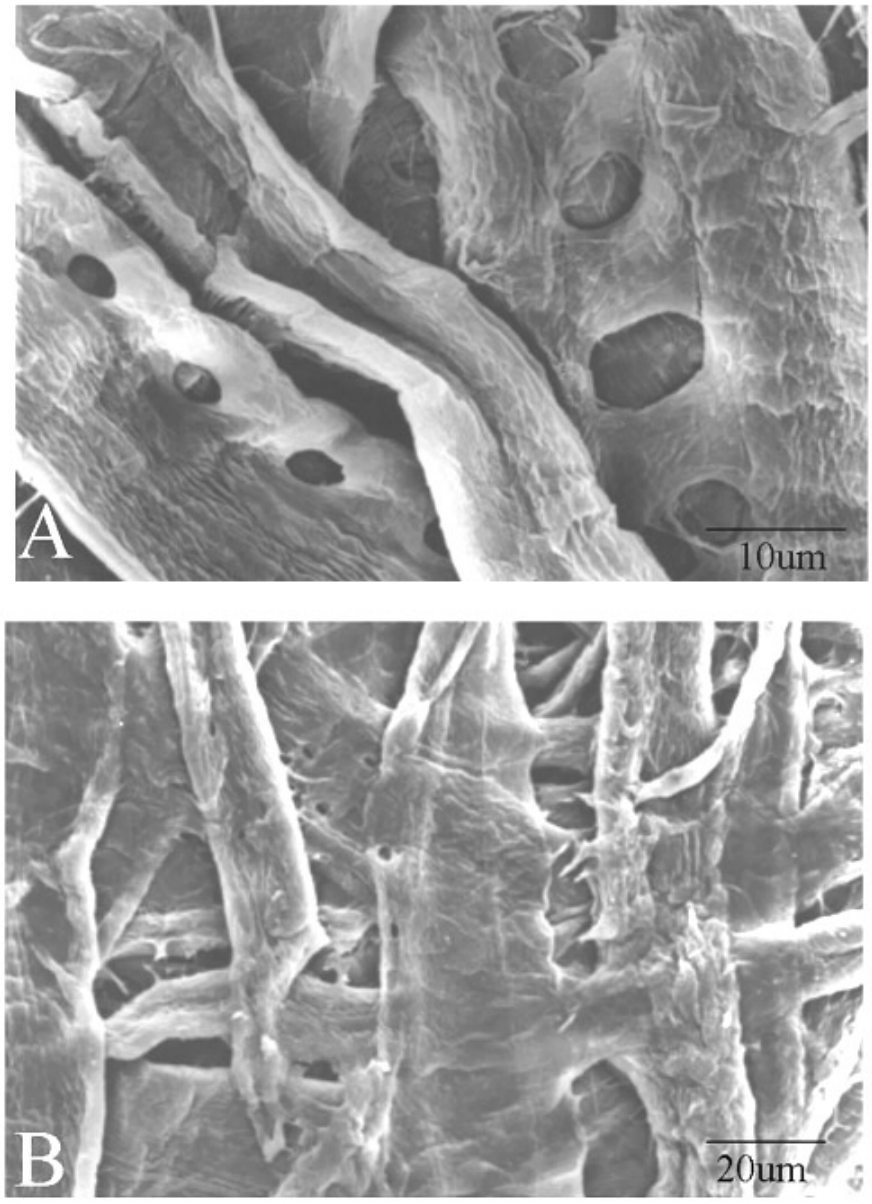


Figure 8.3 SEM micrographs of surface of CPD wet paper treated with 2.0% A) PMA; B) PMMA

the fiber surface show the damage of fiber wall as a result of beating. The fibers in the paper treated by high molecular weight PMMA are adhered together by the added polymer. This is an evidence that the bulky PMMA macromolecules tend to stay on fiber surface, move to the crossing area of fibers under the action of surface tension and capillary force, increase fiber contact area and produce predominately fiber-polymer-fiber bonds. The inter-fiber crosslinks reinforce and protect the fiber-fiber hydrogen bonds from dissolution in water.

Tensile Fracture of Dry Paper

The edge viewing of tensile fracture of control sample and PMA-treated paper are exhibited in micrographs A and B in Figure 8.4, respectively. As shown in the micrographs, the dry fracture of control sample results mainly from the pulling out of fibers, while dry fracture of PMA-treated sample results in breakage of many fibers. For untreated control sample, the fibers are strong enough to withstand the stress, and the tensile strength is determined by the interfiber hydrogen bonds. While PMA treatment produces cross-links inside of fibers, restricts mobility of fiber components, and results in the stress concentration and embrittlement of fibers. Therefore, more fibers are broken during tensile fracture. The increased brittleness directly leads to a reduced stretch, premature breakage, reduced tensile energy absorption, diminished folding endurance, and even deteriorated dry strength [11].

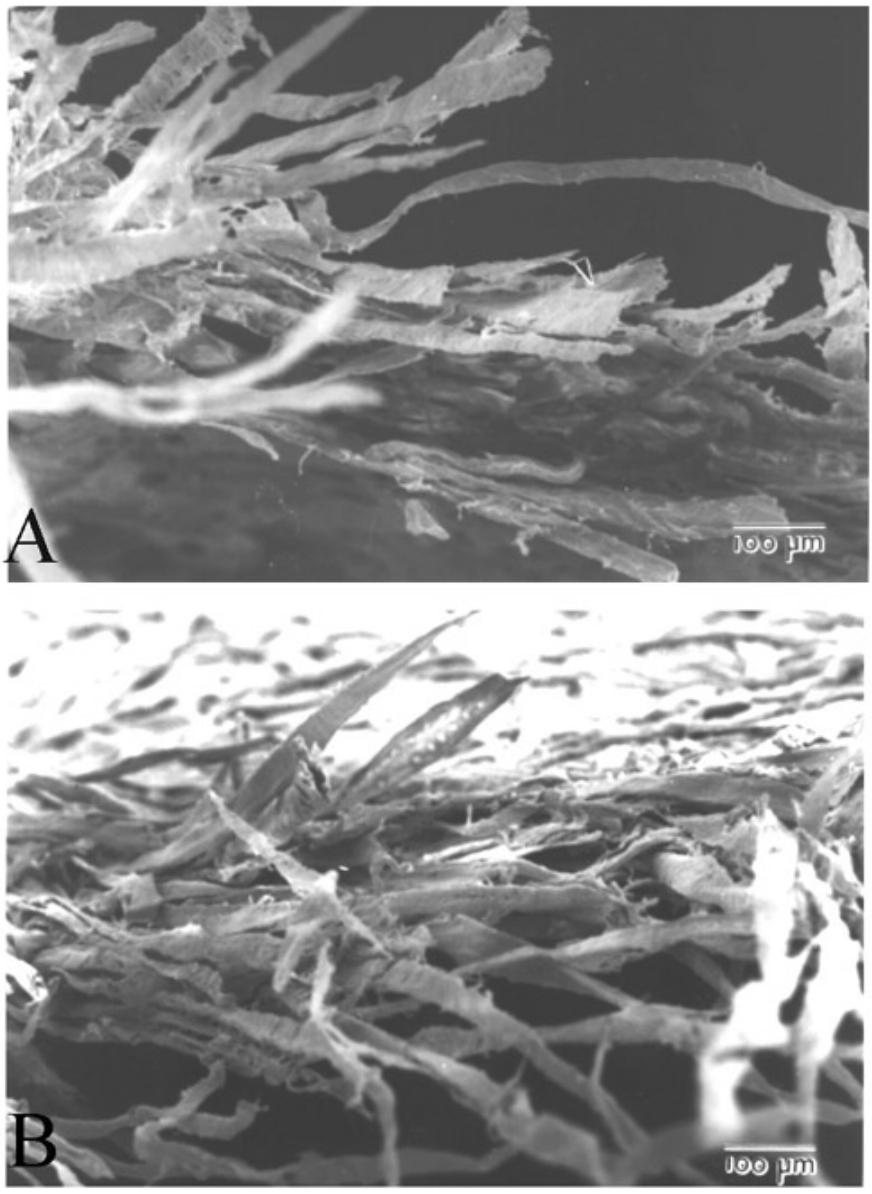


Figure 8.4 SEM micrographs of tensile fracture of dry paper: A) Control; B) Treated with 2.0% PMA

Swelling, Water Retention, and Internal Bonding of Paper Treated with Glutaraldehdye and Poly(vinyl alcohol)

Fiber Swellability and Paper Thickness

Swelling is a characteristic closely associated with moisture-related physical properties and chemical reactions in most cellulosic substrates [25]. Cellulosic fibers consist of a large number of discontinuous crystalline regions separated by amorphous regions of cellulose macromolecules with fairly strong inter-chain hydrogen bonds. The swelling behavior is dictated to a great extent by these inter-chain bonds. Liquid water enters paper by two approaches [26]. Liquid water flows into the interfiber capillaries and proceeds through the thickness of the paper sheet at a rate depending upon the amount of sizing. Meanwhile, water penetrates into the fiber wall and exerts an osmotic pressure that causes the fibers to swell. Water molecules penetrate into inter-lamellae and inter-fibrillar non-crystalline regions through very fine submicroscopic channels, break the hydrogen bonds between the neighboring cellulose molecules by replacing with their own hydrogen bonds with the macromolecules, and loosen the structure of the fibers.

Figure 8.5 presents the dry and wet thickness of paper treated with 2.0% glutaraldehyde with and without addition of 1.0% PVA, pH 4.3, cured at 120, 130, 140, and 150^{o}C for 1.5 min. The thickness is shown as function of W/D ratio. One observes three phenomena from the figure. Firstly, the addition of 1.0% PVA improved the wet strength of glutaraldehyde-treated paper with a W/D ratio of 10% higher magnitude, thus reducing the curing temperature for about 10^{o}C. Secondly, the paper treated with glutaraldehyde/ PVA is thicker in both dry and wet states than that treated with glutaraldehyde alone. Thirdly, as curing temperature was raised and wet strength

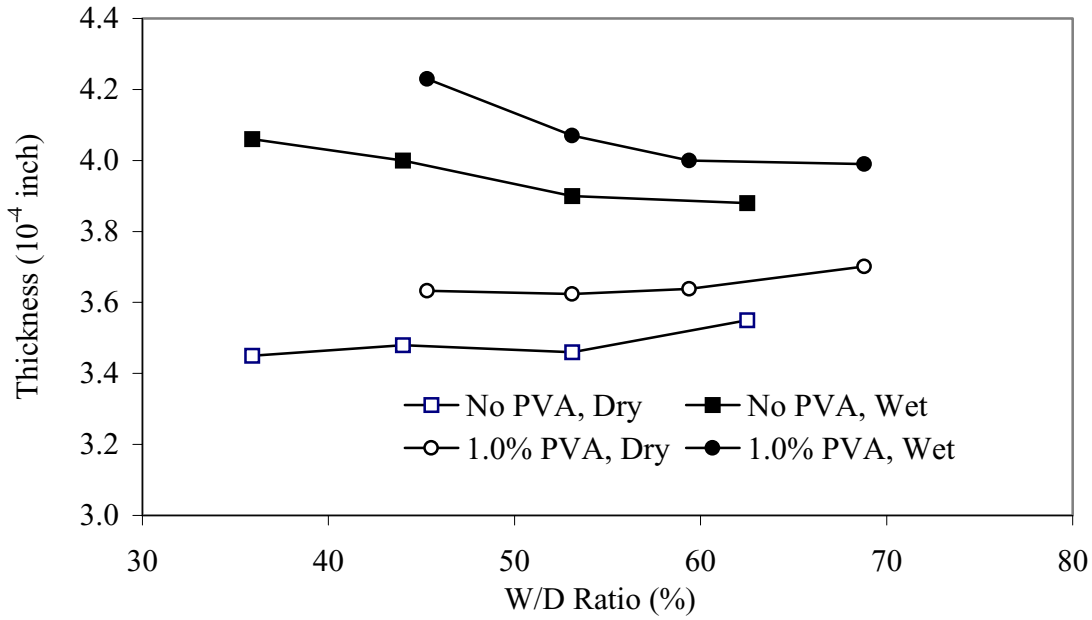


Figure 8.5. Dry and wet thickness shown as a function of wet strength, paper treated by 2.0% glutaraldehyde with and without addition of 1.0% PVA, pH 4.3, cured at 120, 130, 140, and 150°C

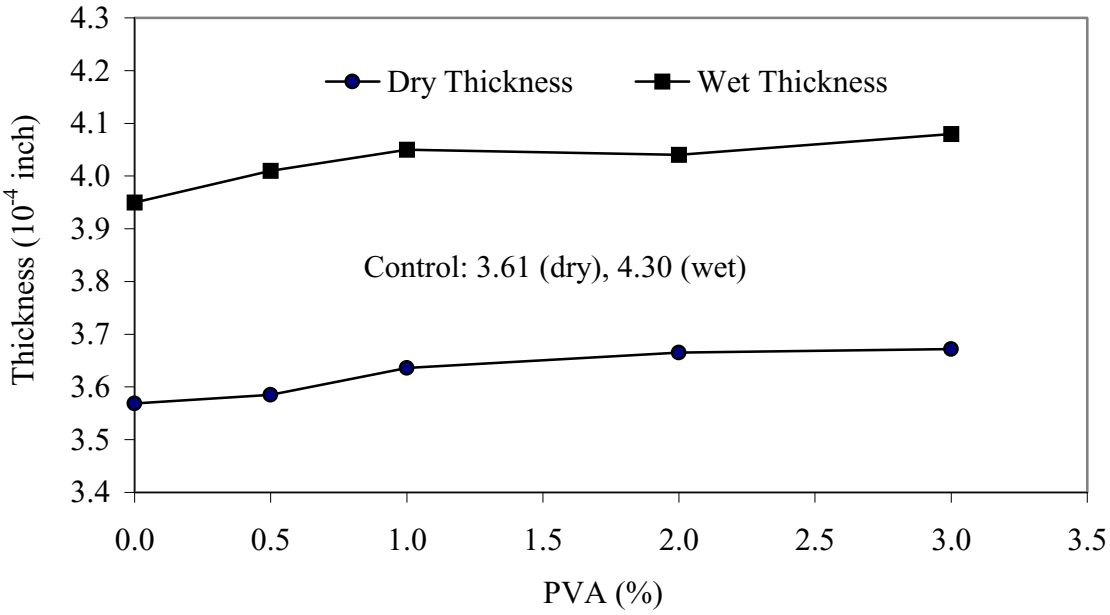


Figure 8.6. Dry and wet thickness shown as a function of wet strength, paper treated by 2.0% glutaraldehyde with various additional amounts of PVA, pH 5.3, cured at 140°C

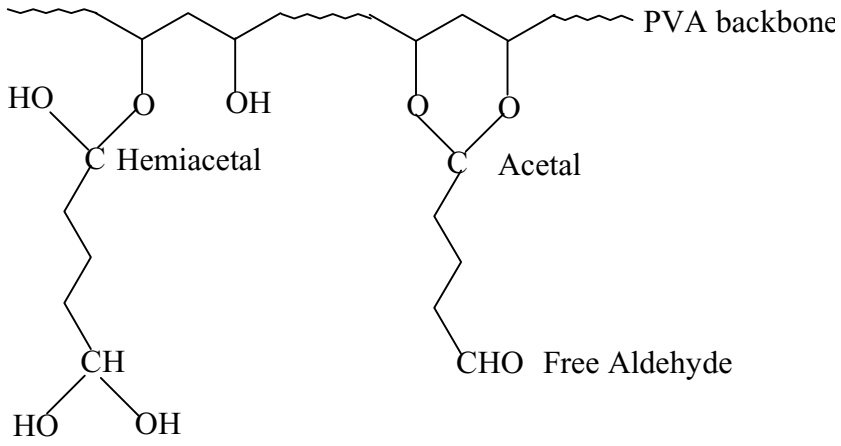
increased, the wet thickness decreased, while the dry thickness of treated paper increased slightly.

Figure 8.6 displays the thickness of paper treated with 2.0% glutaraldehyde in combination with different amounts of PVA. Both dry and wet thickness increases as additional amount of PVA is increased.

It is the covalent acetal cross-links between adjacent cellulose chains that reduces the swelling of fibers and improves the wet strength of paper. The cross-linking network restricts the accessibility and swelling of fiber network by water, protects the inter-fibrillar, inter-lamellae, and inter-fiber hydrogen bonds from disruption by water, and thus retains the strength of paper sheet. Theoretically, if the reactants penetrated into fibers to an appreciable extent and crosslinking took place throughout the fibers, the swelling of paper should reduce progressively as wet strength increases.

The combination of PVA into the crosslinking system increases both wet strength and swellability of the treated paper as shown in Figure 8.5. The fact indicates that the combination of PVA into the crosslinking system as a co-reactant optimizes the distribution of crosslinks among the fiber network and improves the efficiency for protecting interfiber hydrogen bonds while reduces the restrain of mobility of micro-structural components of cellulosic fibers. One reasonable interpretation of this phenomenon is that PVA reacts with glutaraldehyde and chains up the small glutaraldehyde to form a bulky complex, or pentanedialated-PVA, as shown in Scheme 1. With appropriate ratio, the pentanedialated-PVA carries highly reactive aldehyde and hemiacetal groups, which can react with cellulose or PVA to created a three-dimensional crosslinking network. Because of its bulky molecular size, the pentanedialated-PVA

cannot penetrate into fiber interior easily but stays on fiber surface and fiber crossing area to increase fiber contact area and produce interfiber crosslinks, it may also partly diffuse into large pores and voids in the fiber surface to improve fiber-resin interaction. Little reaction taking place inside of the fibers leads to less restriction on mobility of fibrous micro-components and less restrain on the fiber swelling. As result, pentanedialated-PVA not only shows high efficiency for improving wet strength than glutaraldehyde, but also improves dry strength and folding endurance of treated paper [14, 15].



Scheme 1. Pentanedialated-PVA

Another evidence of PVA involving in the crosslinking of cellulose can be found from the effect of additional amount and molecular weight of PVA to the wet strength of treated paper. As shown in Figure 8.8, wet strength increases with increasing amount of PVA. If PVA didn't involve in the reaction between cellulose and glutaraldehyde, it would make only limited contribution to wet strength even though it can increase dry strength to some degree, according to the protection mechanism of wet strength [27]. The wet strength of treated paper also increase with molecular weight of PVA [15].

Treatment by glutaraldehyde alone decreases the thickness of dry paper (Figure 8.5). The reducing paper thickness arises from the shrinking of cellulosic fibers due to crosslinking. The shrinking could result from the collapse of pores or fusion of lamellae as a result of hemiacetal or acetal crosslinks inside the fibers. When PVA is combined as a co-crosslinker of glutaraldehyde, the treated paper shows a similar or slightly increased dry thickness compared to the control sample. The result is possibly also attributed to the little depth of penetration of the pentanedialated-PVA into the fibers and fewer intrafiber crosslinks. The slight increase in dry thickness as curing temperature increased is possibly due to the increased stiffness of treated paper at higher curing temperatures. As illustrated in Figure 8.6, both dry and wet thickness of paper treated with 2.0% glutaraldehyde increase slightly as the additional amount of PVA is increased.

Water Retention

Another phenomenon accompanying the swelling of cellulosic substrate is the water retention. The sorption of water by cellulose substrate is generally considered as surface adsorption, and the sorption capacity of the fiber is related to its "internal surface". [17]. There are two types of sorbed water: 1) water whose energy of binding to the cellulose is higher than the energy of interaction between the molecules of water; 2) water which has condensed inside the cellulosic structure without a thermal effect. The sorption of water reflects the submicroscopic structure of fibers. As water is attached to fiber surface as well as imbedded inside the capillaries, in order to measure the true water content in the fiber wall, it is necessary to remove the mechanically held water from capillary and inter-fiber areas [26]. The centrifuge method is designed for the purpose [23].

Figure 8.7 shows the water retention of paper treated with 2.0% glutaraldehyde with and without addition of 1.0% PVA and cured at 120, 130, 140, and 150^{o}C for 1.5min. The water retention is expressed as a function of W/D. The control sample had a water retention of 83.0% and a W/D ratio of 10.0%. Because cross-links reduce the water sorption of fibers, the water retention of paper decreased with increasing wet strength in both cases. However, based on the same wet strength, the paper treated with glutaraldehyde/PVA exhibited a water retention 5.0 to 8.0% higher than that treated with glutaraldehyde alone. The result indicates that addition of 1.0% PVA increased wet strength of paper with less reduction of moisture sorption.

Figure 8.8 presents the water retention and wet strength of paper treated with 2.0% glutaraldehyde as a function of additional amounts of PVA. It is seen from the data that the water retention increased from 51.6% to 56.7% and wet strength increased from 51% to 71% as addition of PVA increased from 0.0% to 3.0%. An increase in the amount of added PVA increases the wet strength of paper crosslinked by glutaraldehyde. The uptake of water is an indication of the loosening of the fiber wall structure [28]. Water sorption of paper generally decreases with increasing wet strength. If PVA molecules were able to penetrate into the fiber wall to an appreciable extent and wet strength increased as a result of cross-links formed throughout fiber wall and interfiber areas, the swelling of fibers and thus the thickness of wet paper would be greatly reduced as a result of improved wet strength. The experimental data presented in Figure 8.8 suggests the contrast. Therefore, the most reasonable interpretation is that PVA directly attends the reaction between glutaraldehyde and cellulose and renders the crosslinking reaction to take place predominately in the shallow surface of fibers and interfiber area.

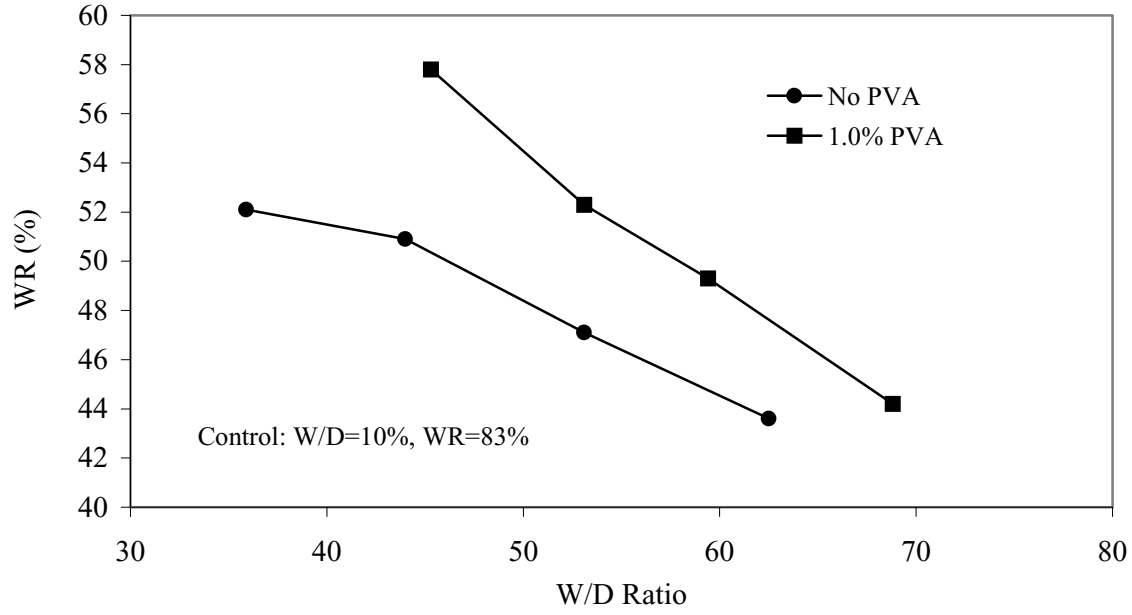


Figure 8.7. Water retention (WR) of paper treated by 2.0% glutaraldehyde with and without addition of 1.0% PVA, pH 4.3, cured at 120, 130, 140, and 150^{o}C

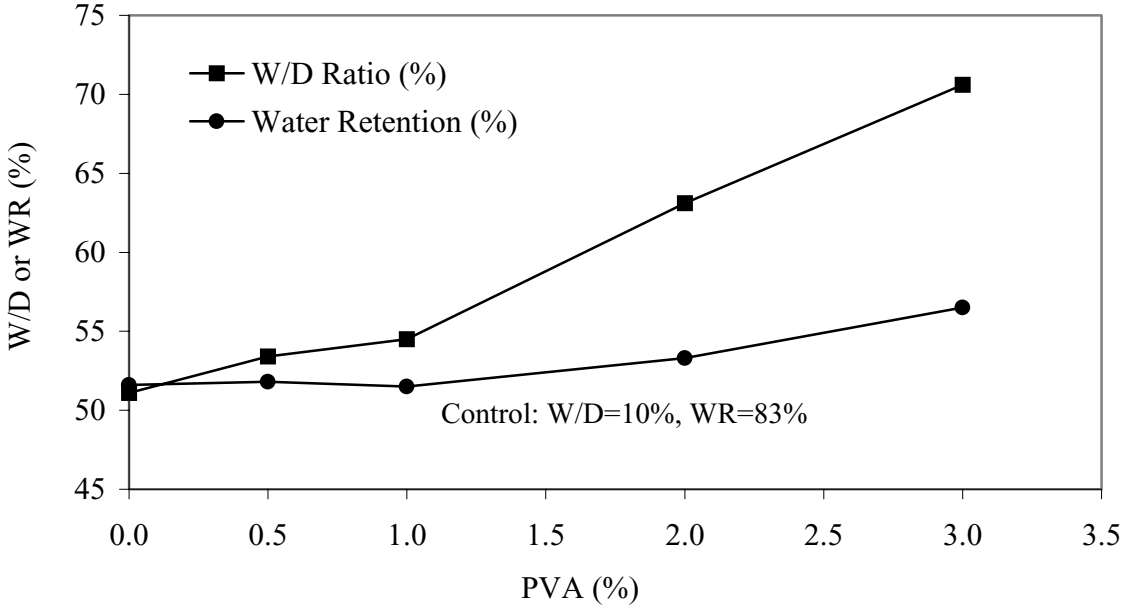


Figure 8.8. Water retention (WR) and wet strength (W/D) of paper treated by 2.0% glutaraldehyde with different amounts of PVA, pH 5.3, cured at 140^{o}C

Internal Bonding (Z-direction Tensile Strength)

Fiber bonding is the most important factor determining the structure and properties of paper. The number and area of bonds affect most of the fundamental properties of paper, including optical, mechanical, thermal, and electrical properties [29]. The extent, intensity, and nature of fiber bonds are thus of vitally importance to paper properties. Previous studies [14, 15] and the aforesaid discussion suggested the glutaraldehyde/PVA cross-linking system produces predominantly shallow surface and inter-fiber cross-links, which will definitely improve fiber-fiber bonds.

Z-direction tensile strength is most frequently used to characterize the fiber-fiber bonds of paper [29]. The Z-direction tensile strength of paper treated with 2.0% glutaraldehyde with and without addition of 1.0% PVA at pH 4.3 and cured at 120, 130, 140, and 150^{o}C is shown as function of wet strength in Figure 8.9. One observes that the glutaraldehyde/PVA-treated paper possessed a Z-direction tensile strength 5.0 to 8.0 psi higher than that treated with glutaraldehyde alone. Figure 8.10 shows the Z-direction tensile strength of paper treated with glutaraldehyde increased from 107 psi at no addition of PVA to 122 psi with addition of 3.0% PVA. As discussed above, the increase in Z-direction tensile strength is attributed to the improvement of fiber-fiber bonds. It offers the papermakers an extra benefit to maintain and upgrade sheet specifications at lower cost, because they can use lower basis weights, higher filler contents, more hardwood fiber, and more secondary fiber to make paper.

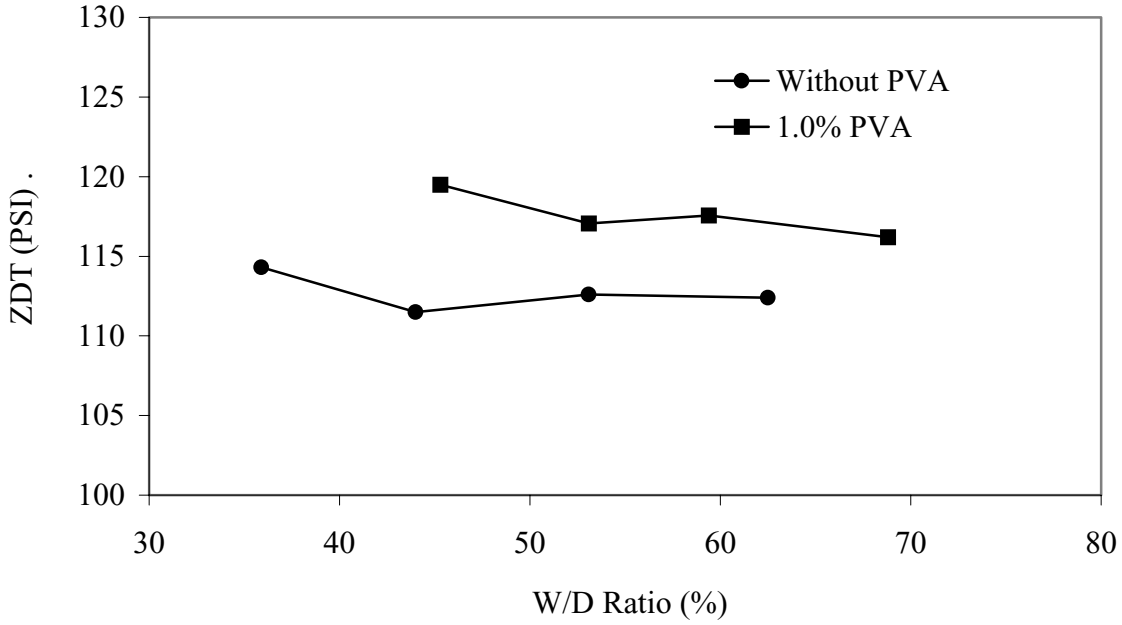


Figure 8.9. Z-direction tensile strength shown as a function of wet strength, paper treated with 2.0% glutaraldehyde with and without addition of 1.0% PVA, pH 4.3, cured at 120, 130, 140, and 150°C

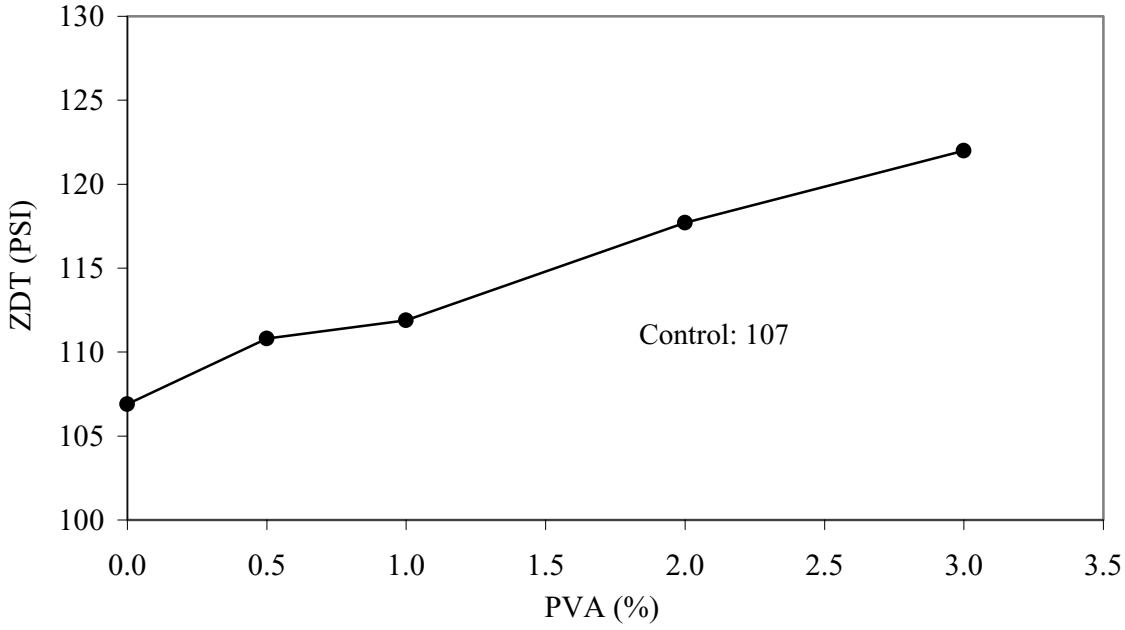


Figure 8.10. Z-direction tensile strength of paper treated by 2.0% glutaraldehyde with various additional amounts of PVA, pH 5.3, cured at 140°C

CONCLUSION

The study reveals some mechanisms of paper wet strength imparted by polycarboxylic acids and glutaraldehyde/poly(vinyl alcohol). The distribution of crosslinks in the fiber network can be examined microscopically and studied by the swelling, water retention, and Z-direction tensile strength of treated paper. The maleic acid copolymer of high molecular weight tends to produce crosslinks predominantly in interfiber areas, while poly(maleic acid) of low molecular weight produces predominantly intrafiber crosslinks. Poly(vinyl alcohol), used as co-crosslinker for glutaraldehyde, directly participates in the reaction of cellulose with glutaraldehyde. The combination of PVA and glutaraldehyde promotes the formation of interfiber crosslinks, enhances the efficiency of the crosslinking system for improving wet strength, and improves the dry strength and folding endurance of paper.

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CHAPTER 9

CONCLUSIONS

1. Improving wet strength of paper with polycarboxylic acids

Polyfunctional carboxylic acids possess high reactivity to cellulose and show high efficiency for improving wet strength of paper. The polycarboxylic acids, including low molecular weight poly(maleic acid) (PMA) and high molecular weight maleic acid copolymers such as poly(methyl vinyl ether-co-maleic acid) (PMMA), are potentially environmentally-friendly alternatives for the current commercial wet strength resins. Both PMMA and PMA demonstrate comparable effectiveness in improving wet strength and wet stiffness of paper. However, PMMA treatment provides significant improvement in dry strength, tensile energy absorption and folding endurance, and slight increases in the stretch of the treated paper. In contrast, PMA treatment causes severe reduction in stretch, tensile energy absorption and folding endurance. Paper treated with PMMA shows a lower energy to yield point than that treated with PMA. Scanning electron microscopic observation also reveals that fibers in PMA-treated paper are swollen to less extent when soaked in water than those in PMMA-treated paper.

The striking difference in the properties of paper treated with these two polymeric carboxylic acids is attributed to the difference in their molecular sizes. High molecular weight PMMA favors formation of inter-fiber crosslinks, thus improving dry strength and toughness. Low molecular weight PMA produces predominantly intra-fiber crosslinks, thus causing embrittlement of fibers, and diminishing flexibility of the treated paper. Polycarboxylic acids share the same drawback in that they require a curing temperature as high as 170^{o}C for efficient reaction.

2. Improving wet strength of paper with polycarboxylic acids and poly(vinyl alcohol)

The use of fully hydrolyzed PVA as a co-additive enhances the performance of poly(maleic acid) as a wet-strength agent of paper. The addition of PVA provides significant improvement in dry strength and wet strength, as well as the folding endurance of the paper crosslinked by PMA. This is probably due to the enhancement of fiber-to-fiber bonding by the reaction between PMA and the high molecular weight PVA.

3. Improving wet strength of paper with dialdehydes

Glyoxal and glutaraldehyde show strikingly different reactivity toward cellulose and thus their performance for improving the wet strength of paper. Glyoxal is able to react with cellulose to form hemiacetal bonds without the aid of a catalyst and elevated temperatures and provides temporary wet strength to paper. The use of $Zn(NO_3)_2$ as a catalyst improves the durability of the wet strength rendered by glyoxal to some extent, but it also causes severe embrittlement and loss of folding endurance of the treated paper. Without a catalyst, glutaraldehyde is not able to bring about any wet strength to paper even under elevated curing temperatures. In the presence of a catalyst such as $Zn(NO_3)_2$, glutaraldehyde becomes very efficient in crosslinking cellulose and thus greatly improves durable wet strength. Glutaraldehyde is also able to retain stretch and folding endurance of the treated paper until relatively high wet strength level. Compared to the paper treated with glyoxal, the paper treated with glutaraldehyde exhibits both higher level of wet strength and higher retention of its flexibility. Dialdehydes show an advantage over polycarboxylic acids in their low curing temperature around 120^{o}C.

4. Improving wet strength of paper with glutaraldehyde and poly(vinyl alcohol)

The crosslinking system, i.e., glutaraldehyde/PVA/catalyst, possesses high efficiency for improving wet strength, dry strength, and folding endurance of paper under low curing temperature around 110^{o}C. The combination of PVA as a co-additive not only improves wet strength but also significantly increases dry strength, stretch, tensile energy absorption, and folding endurance of the paper crosslinked by glutaraldehyde. The wet strength of treated paper increases with both additional amounts and molecular weight of PVA. Addition of PVA also improves the water absorption of paper crosslinked by glutaraldehyde. The swelling and water retention of treated paper increases gradually with the increasing addition of PVA.

Meanwhile, glutaraldehyde is superior to glyoxal for improving durable wet strength without sacrificing dry performance of treated paper. Moreover, $Zn(NO_3)_2$ is one of the highest efficiency catalyst in promoting the crosslinking acetalization of pulp cellulose by combination of glutaraldehyde an PVA. It remains effective in acidic and neutral papermaking conditions.

It is believed that poly(vinyl alcohol) directly participates in the reaction of cellulose with glutaraldehyde. The excellent performance of the crosslinking system results from the formation of an interfiber crosslinking network through the reaction of glutaraldehyde to both PVA and cellulose. The combination of PVA and glutaraldehyde promotes the formation of interfiber crosslinks, thus showing high efficiency for improving wet strength and dry properties.