Dry Strength: Strategies for Stronger Paper

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7.1. INTRODUCTION

The dry strength of paper can be defined as the ability of a dry paper specimen to resist a variety of external forces. Common paper dry strength properties can be grouped into in-plane strength properties, out-of-plane strength properties, and structural mechanical properties, based on the type of external force.

Paper is a web of cellulose fibers. Many of the strength properties of paper are directly related to fiber packing density, bonding strength among fibers, and the strength of individual fibers. Paper strength is also a function of paper’s uniformity of formation. Failure modes for dry paper are often initiated from a defect-based heterogeneity in sheet structure.

This chapter focuses on the various chemical approaches to intensify inter-fiber bonds. By strengthening these bonds, the overall paper product is imparted with more desirable characteristics. To begin the discussion, the next section describes some of the key challenges that modern papermakers face with regards to paper strength. The third section concerns the ways in which paper fails, along with methods for the evaluation of paper strength. The final two sections deal with conventional and non-conventional ways to increase paper’s strength, again with the emphasis being placed on the use of chemical additives at the paper machine wet end.

7.2. CHALLENGING CIRCUMSTANCES FOR PAPER STRENGTH

The paper industry has developed several different strategies to optimize paper dry strength properties. Stronger paper can be produced by increasing paper basis weight, which is the weight per unit area of paper. However, because the cost of wood is a large portion of the total cost of making paper, simply increasing basis weight is rarely cost-effective. Desirable dry-strength properties are often achieved by balancing the use of dry-strength chemical additives and optimization of papermaking process mechanics.

Lightweighting is an ongoing trend in the industry. This term is used when paper companies prefer to maintain the existing strength properties while lowering paper basis weight.

A variety of trends in the industry can lead to reduced paper strength. These approaches include increasing contents of fillers [Li et al. 2002] and increased usage of higher-yield fibers. Both of these trends are motivated by the desire to decrease fiber costs. Specifically, kraft fibers produced at a relatively high yield (~61%) exhibit distinctly lower paper strength properties compared with the corresponding fibers pulped to a more typical yield (57%) [Gärdlund et al. 2005]. Furthermore, high-yield pulps, such as groundwood and thermomechanical pulp (TMP), often must be complemented by kraft fibers to meet the final paper strength requirements [Korpinnen and Fardim 2009].

In addition to trends of high-yield pulp and filler content there is a growing number of paper products being produced utilizing recycled fiber sources. A significant portion of container board product is produced using old corrugated container (OCC) pulp, which is a recycled pulp from used brown container board. In many cases, the OCC pulp has gone
through multiple cycles of the recycling process. Figure 7.1 demonstrates how paper strength properties can change during several cycles of paper forming, drying, usage, and repulping [Cabalova et al. 2011]. If refining is included in each cycle, then the fiber length and inherent strength are also negatively impacted. In addition, the swelling propensity of wood fibers is decreased with increased cycles of recycling. This leads to reduced bonding area among wood fibers.

** PLACE FIGURE 7.1 NEAR HERE **

It is well known that increasing environmental and economic awareness have motivated papermakers to reduce the amounts of fresh water per ton of paper being produced [Bourgogne et al. 2001]. As a result, paper mills are striving to recirculate a higher percentage of water to pulping and wet end operations. A higher level of water recirculation can lead to buildup of electrolytes, wood resins, and chemical additives in the water system. Figure 7.2 demonstrates the buildup of electrolytes as the number of recycling increases. Unfortunately, these factors can impact the performance of dry-strength additives. As a result, papermakers are continuously searching for new dry-strength additives that demonstrate more tolerance to closed water systems.

** PLACE FIGURE 7.2 NEAR HERE **

Another challenge to paper strength is moisture in the air. High-humidity conditions can greatly reduce the ability of paper and paperboard to withstand various loads and stresses [Bandyopadhyay et al. 2000]. Unstable values of relative humidity have been shown to contribute to progressive distortion, possibly leading to failure of boxes [Byrd 1972; Alftan 2004].

7.3. HOW PAPER FAILS AND HOW TO TEST IT

7.3.1 Paper Testing Principles

In-plane strength properties measure paper strength parallel to the surface of the paper plane. One of the most commonly tested in-plane strength properties is tensile strength in either the machine direction (MD) or cross-machine direction (CD). Tensile strength in various grades of paper is important for a wide range of reasons. For example, the need for printing papers to meet a tensile strength target is based on the necessity of maintaining the sheet dimensional stability during the printing process. In packaging grades, such as sack and bag grades, achieving a high tensile ensures that the bag content can be carried. Interestingly, tissue grades often have both a low and a high limit for tensile strength. Specifically, tissue products with a weak tensile strength can fail easily and will not fulfill their designed functions. On the other hand, tensile strength is inversely related to tissue softness, and excessive tensile strength will result in stiff tissue products with undesirable tactile feel characteristics.

Out-of-plane strength properties measure the ability of paper to withstand tensile stress perpendicular to the surface of the paper. This type of strength property is important in processes such as offset lithography where use of tacky ink can split paper. Out-of-plane strength is also important in packaging boards with multi-ply layers to ensure the layers do not fail under load. For coating papers, the escaping water vapor during the drying process produces high z-direction delamination stress forces. This can
result in undesirable defects in the form of blisters. Examples of popular out-of-plane strength measurements include Scott bond, z-direction tensile, and plybond.

Structural mechanical properties are important for packaging and board paper grades. When paper boxes are stacked on top of each other, it is critical to maintain their original structures to protect the content inside them. The key strength properties in this application are edgewise compressive strength and bending stiffness. Edgewise compressive strength measures the compressive force required to buckle the paper sample along the edgewise direction. In comparison, bending stiffness is the load required to bend the paper sample. As shown in the following sections, both edgewise compressive strength and bending stiffness are closely related to the crush strength of board products.

The selection of dry-strength additives often requires careful laboratory study and paper machine trials. The paper industry has used natural gums and starches for centuries and has also developed synthetic dry-strength resins over the past several decades. The performance of dry-strength additives directly depends on wood fiber source and the type of paper machine. It is also critical to ensure that all wet-end chemicals function at the best possible levels. Consequently, selection of dry-strength additives requires a thorough understanding of both the paper machine operation and the papermaking additives being used in the process. Paper dry-strength additives have been previously reviewed [Pelton 2004; Lindström et al. 2005].

7.3.1.1. In-Plane Tensile Strength

In-plane tensile strength is undoubtedly one of the most studied paper strength properties. It is closely monitored during the production of many paper products, such as printing and writing paper and tissue paper. This strength property impacts both paper quality and subsequent printing and converting processes. A paper web with proper tensile strength is critical for smooth continuous production of high-quality finished paper goods. Furthermore, tensile strength is closely related to other strength properties.

In a typical paper tensile strength test, a paper sample with a set width is elongated at a predetermined speed [Levlin 2008]. Tensile load is then recorded as a function of paper strain. Tensile load is defined as the elongation force per unit width of paper sample, and strain is defined as the percentage of elongation as compared with the original length of paper sample. The paper sample will continue to elongate until it breaks. Figure 7.3 demonstrates a typical load-displacement curve of a paper tensile test. The tensile load at failure is defined as paper tensile strength ($S_t$). In addition, several other key parameters are calculated from the raw data. The maximum slope of the stress-strain curve is used as the elastic modulus of paper ($E$). The area below the stress-strain curve is defined as tensile energy absorption ($TEA$), which is a measure of the total work required to rupture the paper sample.

** PLACE FIGURE 7.3 NEAR HERE**

Paper tensile strength is a complex property, and its prediction has been studied both microscopically and macroscopically. The Page equation is probably the most widely used equation to correlate paper tensile strength with paper microscopic properties [Page 1969].

Page made two important assumptions in his well-known published paper. The first assumption is that paper tensile strength is dependent on individual fiber strength and bond strength between fibers. When paper breaks under elongation, fibers along the
rupture line can be divided into two fractions. The first fraction breaks under elongation load. The second fraction of fibers remains intact. The elongation load only breaks their bonding with other fibers, and they simply pull out of the fiber network. The second assumption is that the number of fibers from the first fraction to the number of fibers from the second fraction is only dependent on the ratio of fiber strength to inter-fiber bonding strength. Under these assumptions, Page was able to develop a simple mathematical equation (Eq. 1) to predict paper finite-span tensile strength $T$,

$$\frac{1}{T} = \frac{9}{8Z} + \frac{12A\rho}{bPL(RBA)}$$  (1)

where $Z$ is the zero-span tensile strength that is directly related to fiber strength, $A$ is the average fiber cross-section area, $\rho$ is the density of the fiber (kg/m$^3$), $b$ is the fiber shear bond strength per unit of bonded area, $P$ is the perimeter of the fiber cross-section, $L$ is the length of the fiber, and $RBA$ is the relative bonded area.

The two terms to the right of (Eq. 1) correspond, respectively, to fiber failure and inter-fiber bond failure. Important fiber properties include fiber strength and fiber length. An increase of either property leads to higher paper tensile strength. When the fiber attributes are held constant, the remaining important factors that affect interfiber bonding include the shear bond strength $b$ and $RBA$. Increasing either $b$ or $RBA$ leads to higher paper tensile strength.

(Equation 1) is considered as the cornerstone of paper strength mechanism. With the help of (Eq. 1), papermakers can optimize paper tensile strength properties effectively by managing fiber properties and interfiber bonding properties. Wet pressing and refining are two common processes used to adjust RBA. Stronger wet pressing promotes more compact packing and higher RBA. Refining creates more bonding area through internal and external fibrillation of kraft fibers. Refining also makes fibers more flexible and enhances fiber packing density. As shown in the following sections, dry-strength resins are used effectively to increase both interfiber bonding strength and RBA. On the other hand, inorganic fillers and debonders interrupt interfiber bonding [Li et al. 2002].

Recent studies have focused on macroscopic models based on fracture theory. Paper failures are initiated from defect areas, and paper tensile strength is correlated to a macroscopic property, critical fracture toughness. In addition, the fracture theory provides insights regarding why paper fails catastrophically under elongation. A correlation has been observed between fracture energy and paper strength properties [Alava and Niskanen 2008]. This approach provides more insight into some of the observations related to paper failures. Most notably, when a piece of paper breaks under elongation, the fiber network fails catastrophically along the fracture line. Furthermore, paper strength properties are often affected by formation uniformity, which defines how uniformly fibers are distributed in the paper web. Poor uniformity of the sheet is often associated with weaker strength properties. Finally, defects often initiate paper breaks, which happen at a fraction of the predominant tensile strength.

Continuum fracture mechanics predicts that a running paper web usually breaks due to a defect in the paper or a sudden peak in the web tension. Studies have shown that paper typically fails near an existing defect. When the defect becomes a growing crack, elastic energy is released because stress vanishes at the crack faces. Assuming that paper is a linear elastic body, the condition for crack growth is (Eq. 2),
\[ G = \frac{\beta \sigma^2 a}{E'} \geq G_c \]  

(2)

where \( G \) is the decrease in elastic energy per crack area increment, \( \beta \) is a geometric factor that depends the location of the defect, \( \sigma \) is the remote stress far from the crack, \( a \) is the crack length, \( E' \) is the elastic modulus of paper, and \( G_c \) is the fracture energy of paper. Both paper elastic modulus and fracture energy are macroscopic properties. However, they are directly related to many microscopic properties used in the Page equation, such as the individual fiber length \( L \), the shear bond strength between fibers \( b \), and \( RBA \).

According to (Eq. 2), an increase in web tension leads to an increase of elastic energy release rate. At some point, the elastic energy release rate reaches a critical value that is equal to the paper fracture energy. An infinitesimal increment of web tension will cause the crack to grow.

Another term often encountered is paper fracture toughness, \( K_c \), which is defined as (Eq. 3):

\[ K_c = \sqrt{G_c E'} \]  

(3)

The critical web tension can then be defined as (Eq. 4):

\[ \sigma_{app} = \frac{K_c}{\sqrt{a \beta}} \]  

(4)

In reality, paper is not a perfect linear elastic body. There is plastic yielding inside the fracture process zone (FPZ). In addition, even if the defect size goes to zero, the critical web tension will not become infinite as defined in (Eq. 4). As a result, (Eq. 4) is modified as (Eq. 5),

\[ \sigma_{app} = \frac{K_c}{\sqrt{a (\beta + \xi)}} \]  

(5)

where \( \xi \) is the intrinsic FPZ scale to accommodate the plastic yielding inside the FPZ.

The reason that poor formation uniformity gives rise to weak tensile strength can also be explained by fracture theory. Nonuniform formation implies that fibers are distributed unevenly in the paper web. Upon elongation, areas with lighter fiber density deform more considerably and eventually become defects. With further increase of web tension, cracks propagate along those defects, and the paper breaks. In summary, areas with lighter fiber density function as crack precursors.

7.3.1.2. Bending Stiffness

Bending stiffness is a structural strength property associated with both paper structures and paper material properties. Besides individual fiber properties and interfiber bonding properties, structural strength properties also depend on paper thickness and how paper layers are constructed together. Many paperboards products are produced with more than one layer of paper. For example, many carton boards contain three flat layers with the middle layer made of mechanical pulp and the outer layers made of chemical pulp. Container boards, produced either from virgin or recycled pulps, contain a corrugated medium layer sandwiched between two flat outer layers. Such layered structures provide paperboards with higher structural strength properties than a single-layered structure.
Bending stiffness tests measure the resistance to bending of paper and paperboard. One of the most used stiffness testers is the Taber stiffness tester, as shown in Figure 7.4. In a typical test, the upper end of a paper sample is clamped in the vise, which is connected to a pendulum. The lower end of the sample is centered between two rollers with a small distance. As the rollers turn the lower end of the sample, the upper end of paper will deflect to the opposite side. When the upper end deflects to a preset angle (normally 15°), the moment required to turn the lower end of the sample is recorded as the bending stiffness. For each paper sample, the lower end is turned to both left and right directions, and the average of two bending moments is calculated to evaluate sample stiffness.

**PLACE FIGURE 7.4 NEAR HERE**

Bending stiffness is one of the most important paper structural strength properties. When carton boxes are stacked on top of each other, high bending stiffness is required to maintain box integrity. Additionally, bending stiffness is critical to ensure paper machine runnability for various paper grades. For example, proper bending stiffness is required to ensure that paper web remains flat during printing and coating applications. Bending stiffness also needs to be in the right range when paperboard is folded and creased to produce boxes. Paperboard having a bending stiffness that is too high cannot be creased properly. On the other hand, a bending stiffness that is too low will cause poor maintenance of the crease, as well as deviations from flat surfaces. Finally, proper bending stiffness will also ensure that magazines and books remain flat on the display stand. Pages also need to remain firm without feeling droopy during reading.

The bending moment of a single-layered paper, \( S_c \), can be calculated (Eq. 6) by assuming that the paper is a uniform beam [Kajanto 2008],

\[
S_c = \frac{E d^3}{12}
\]  

(6)

where \( d \) is the thickness of paper. It should be noted that the elastic modulus is inversely related to thickness through density. Because the bending stiffness is dependent on the cube of thickness, increasing thickness is a more effective approach to increase stiffness, compared with increasing the elastic modulus. For example, calendaring will increase the elastic modulus but decrease thickness, resulting in a decrease of bending stiffness.

The bending stiffness of a layered paper sample can be calculated by summing the contributions of all layers, if each layer is a uniform beam (Eq. 7),

\[
S_b = \sum_{i=0}^{n} S_{b,i}
\]  

(7)

where \( S_{b,i} \) is the bending stiffness of each layer and given as (Eq. 8),

\[
S_{b,i} = E_i \left[ \frac{d_i^3}{12} + d_i (h_i - z_0)^2 \right]
\]  

(8)

where \((h_i - z_0)\) is the distance between the neural plane of layer \( i \) and the neutral plane of the entire paper. The neutral plane is the plane where there is no strain during bending. In a symmetrical beam, the neutral plane is the middle plane. By contrast, in a nonsymmetrical beam, the neutral plane is more toward the stiffer side.
(Equations 7 and 8) provide papermakers with valuable insights regarding how to design a paper layer structure to enhance bending stiffness. According to (Eq. 8), the contribution of the layer to the bending stiffness is larger if the layer is farther away from the neutral plane. In practice, three-layered paper structures are often used to take advantage of this principle and optimize bending stiffness. The middle layer is commonly produced with bulky fibers, such as mechanical pulp, to increase paper thickness. The outer layers use flexible long fibers, such as kraft pulp, to provide high elastic modulus.

### 7.3.1.3. Edgewise Compressive Strength

Edgewise compressive strength is a critical element in determining the performance of boxes to endure compressive load. Several standard methods have been developed to measure this property. Figure 7.5 shows short-span crush test (SCT) (TAPPI T 826 “Short span compressive strength of containerboard”), ring crush test (RCT) (TAPPI T 822 “Ring crush of paperboard [rigid support method]”), and corrugated crush test (CCT) (TAPPI T 824 CM-14 “Fluted edge crush of corrugating medium [flexible beam method]”), which are commonly used on liner and corrugated medium. The compressive strength of corrugated boards (ECT) is tested using TAPPI standard methods T 811 (“Edgewise compressive strength of corrugated fiberboard [short column test]”), T 838 (“Edge crush test using neckdown”), and T 839 (“Edge compression test for strength of corrugated fiberboard using the clamp method”). ECT can also be estimated from SCT or RCT through a linear length-weighted summation of the individual strengths that make up the board [Popil 2017]. Finally, the crush (compressive) strength of boxes (BCT) is tested using TAPPI standard method T 804 (“Compression test of fiberboard shipping containers”). BCT is a structural strength property, because it is related to both ECT and board bending stiffness.

** PLACE FIGURE 7.5 NEAR HERE

Paper’s compressive strength and tensile strength are closely related to each other, although their mechanisms of failure are different. Like tensile strength, compressive strength is a function of both fiber strength properties and interfiber bonding properties. A close comparison between the compressive stress-strain curve and the tensile stress-strain curve reveals that two curves resemble each other remarkably. Both curves show an initial elastic deformation followed by a plastic deformation. However, paper fails at a much lower strength under compression than under elongation. Tensile breaks are normally caused by fiber failures and inter-fiber bond breaking. Long fibers can be seen pulled out of the fiber network. In comparison, compression failures are typically caused by fiber buckling and separation of fiber bundles.

It is worth noting that more wet pressing and lower paper thickness lead to higher SCT and RCT but lower bending stiffness. Wet pressing enhances interfiber bonding and produces higher RBA. Thus, higher compressive strength is required to separate fibers from each other at the failure point. Unlike compressive strength, bending stiffness is a structural property that depends on both interfiber bonding and paper thickness. Although higher RBA enhances interfiber bonding, it decreases paper thickness. Because bending stiffness is more sensitive to thickness, increased wet pressing often results in lower bending stiffness.

Paper samples with low basis weight often buckle under compression before reaching the compression failure point, resulting in lower compressive strength test results. SCT, RCT, and CCT methods were originally developed to increase the buckling
threshold by using proper specimen geometry. However, paper buckling is only prevented in part in the above tests. The SCT protocol has been shown to produce less buckling and higher compressive strength than RCT. Therefore, SCT is generally considered as the most reliable compression test method.

The crush strength values of boxes depend on both the board bending stiffness and board compressive strength [Kjanto 2008]. There are two main types of paperboards used to produce different kinds of paper boxes. One of them is carton board, which typically has three flat layers. The other type is container board with a corrugated medium and two outer layers (the linerboard). The crush strength $F$ of a rectangular carton board box is calculated as (Eq. 9),

$$F = K \sqrt{\sigma_c d \sqrt{S_{b,x} S_{b,y}}}$$  

where $F$ is the vertical force need to crush the carton board box, $\sigma_c$ is the compressive failure stress that is defined as the compressive failure strength over the cross-sectional area of board, $S_b$ is the bending stiffness in either MD (x) or CD (y), $d$ is the thickness of board, and $K$ is a parameter with a theoretical value of $2\pi$. The crush strength of carton boxes is determined by both compressive failure stress and the geometric mean of the MD and CD bending stiffness. Additionally, this crush strength depends on board thickness, which in turn also affects the bending stiffness. Consequently, board thickness and bending stiffness have more impact on the crush strength of carton boxes than does compressive failure stress.

The crush strength $F$ of a rectangular container board box is calculated as (Eq. 10),

$$F = 2.028 ECT^3 S_{b,geom}^{1 \over 4} z^{1 \over 2}$$

where ECT is the edgewise crush test strength of the board and $z$ is the perimeter of the box. This crush strength is determined by the three-fourths power of compressive strength and the one-fourth power of bending stiffness. Therefore, it is more sensitive to compressive strength. During production, compressive strength is monitored closely for container board grades while bending stiffness is closely monitored for carton board grades.

7.3.1.4. Out-of-Plane Strength

Out-of-plane strength measures the ability of paper to endure tensile stress in the direction of paper thickness ($z$-direction). Like many other strength properties, out-of-plane strength strongly depends on interfiber bonding strength. Factors that increase RBA and interfiber bonding strength will increase out-of-plane strength.

Out-of-plane strength is important for various converting processes and end-use operations. For example, high out-of-plane strength is required for the offset printing process. Otherwise, tacky ink can initiate paper delamination at the printing nip. Another case is in drying, especially in the case of coated products. If the splitting force from the escaping steam exceeds the paper’s delamination strength, blisters will form on the paper sheet. Delamination can also take place easily between the layers of a multiply board because the discontinuity between layers creates weak points.
Z-direction tensile strength (ZDT) (TAPPI T 541 “Internal bond strength of paperboard [z-direction tensile]”) and Scott bond (TAPPI T 569 “Internal bond strength [Scott type]”) are two common standard methods used to measure paper out-of-plane strength. ZDT consists of applying double-sided tape to both sides of a test specimen. The specimen is then placed between two platens and compressed uniformly over the entire specimen surface area. Uniform tension is then applied at a slow and constant rate, and the maximum stress is then recorded. In comparison, Scott bond measures the energy required to rapidly delaminate a paper sheet. The z-direction rupture is initiated by the impact of a pendulum having both a controlled mass and a controlled velocity.

ZDT and Scott bond require the paper specimen to have a minimum basis weight roughly above 60 g/m². Both methods sandwich paper specimen between two double-sided tapes. Adhesive on double-sided tapes will migrate into paper porous structure when the paper specimen is pressed between tapes. At excessively low basis weights, one would just detect the tack of the tape. At high basis weights, ZDT is independent of basis weight, because the specimen fails at its weakest part along the z-direction. In comparison, Scott bond energy increases with the basis weight increase. The increase of Scott bond energy is probably due to energy consumed in specimen plastic deformation and partial rupture throughout the sheet thickness.

7.4. CONVENTIONAL STRATEGIES TO INCREASE PAPER STRENGTH

Although the emphasis of this text is on the role of chemical additives, any discussion of paper strength would be misleading if it did not discuss the dominant role of such aspects as the source of the fibers, the manner or pulping, the refining of the fibers, and some key aspects of the forming, pressing, and drying processes.

7.4.1. Fiber Selection

Aspects of fiber selection, with a view to preparing strong paper, have been addressed in the literature. In particular, Nanko et al. [2010] have documented the attributes of different fiber types.

7.4.2. Pulping

The topic of pulping, with discussion of paper strength aspects, is well covered in the following texts [Biermann 1996; Fardim and Tikka 2011]. Briefly stated, the kraft pulping process is noted for producing fibers that, after removal of lignin, have the potential for strong interfiber bonding after refining (see next item), while maintaining high zero-span tensile strength and other evidence of inherent strength of the individual fibers. Among the mechanical pulping methods, the TMP method is well known for its tendency to preserve fiber length, which is often a key attribute relative to the development of paper strength, especially the tear strength of paper.

7.4.3. Refining

In the case of kraft pulps and other delignified pulps, the strength potential is not fully realized until after the wet fibers have been subjected to mechanical forces (i.e., the refining process) [Biermann 1996; Gharekhani et al. 2015]. Briefly stated, during the refining process a fiber encounters repeated shearing and compression forces that partly
delaminate the cell wall and cause it to adopt a more ribbonlike cross-section. The relative bonded area between fibers within paper [Page 1969] is greatly increased during refining.

7.4.4. Forming, Pressing, and Sheet Handling

To be strong, paper needs to be composed of fibers that are relatively straight, suitably distributed, suitably oriented, have an optimized density, and then be dried under suitable constraint to avoid excessive shrinkage of the paper [Setterholm and Kuenzi 1970; Byrd 1981; Ostlund et al. 2004]. For example, the tension within the web of fiber during the drying process can result in straighter fibers within the final paper, and this can be important for dimensional stability and various strength attributes [Page and Tydeman 1962]. Thus, the paper machine equipment, as well as its optimized use, is of paramount importance. Without careful attention to such factors, application of chemical additives to meet paper strength objectives (see next section) is unlikely to achieve satisfactory results.

7.4.5. Dry-Strength Additives and Their Strategic Use

When viewed in the context of optimized fiber selection, pulping processes, sheet forming, wet pressing, and maintenance of tension during drying, one can view the role of dry-strength additives as a way that papermakers can often achieve yet an additional increment of paper strength. This section first considers some key findings that have helped paper technologists understand the various mechanistic roles of dry-strength additives. Next, there is focused discussion regarding glyoxylated polyacrylamide dry-strength agents, followed by a discussion of permanent wet-strength additives, which can be considered in strategies to achieve higher strength gains compared with earlier generations of dry-strength additives. Next is a discussion of starches, especially cationic starch products, which have a long history as a major strength additive for wet-end addition. Other classes of dry-strength additives discussed in this section are polyvinylamines, anionic acrylamide copolymers (as complexes with cationic additives), amphoteric products, and carboxymethyl cellulose (CMC).

7.4.5.1. General Considerations

The application of dry-strength additives is an effective way to optimize paper dry-strength properties. Commonly, the word “resin” is interchangeable with the word “additive” when discussing dry-strength additives. Resin refers to a wide variety of polymeric products that can enhance the interaction among cellulose fibers. Commercial dry-strength resins are either water soluble or water dispersible. They are typically applied in liquid form either to the pulp suspension at the wet end or on wet sheet surface post-sheet forming.

For wet-end addition, dry-strength resins normally carry ionic charges. The ionic interaction between dry-strength resins and a cellulose fiber surface is a driving force to retain dry-strength resins in paper. Cationic dry-strength resins can adsorb onto anionic fiber surface directly. Anionic dry-strength resins require a cationic additive to promote their retention with fiber. Surface-applied dry-strength resins do not require ionic charges.

The detailed mechanisms of various dry-strength resins have long been an area of debate. Paper pulp suspensions are rather complex systems, containing various types of
cellulose fibers, fines, inorganic fillers, ions, and process chemicals. In addition, dry-strength resins cover a wide range of synthetic and natural chemicals. Furthermore, conflicting experimental results have been reported in the literature. In this chapter the objective is to summarize basic paper dry-strength mechanisms while recognizing that many alternative explanations can be found in the literature.

It is generally believed that dry-strength resins enhance paper strength by enhancing interfiber bonding properties rather than strengthening individual fibers. Increasing the RBA and interfiber bond strength are two dry-strength resin mechanisms proposed in the literature. Most dry-strength resins are believed to increase paper dry strength through both mechanisms [Lindström et al. 2005]. In addition, Lindström et al. [1985] proposed that certain dry-strength resins decrease the buildup of stress concentrations during drying.

Commercial dry strength resins can be divided into reactive resins and nonreactive resins. The interaction between reactive strength resins and cellulose are of chemical nature with covalent bond formation. In contrast, the interaction between nonreactive strength resins and cellulose are of physical nature with hydrogen-bond formation.

The primary mechanism of reactive strength resins is through strengthening interfiber bonds with strong covalent bonds. The bond energy of hydrogen bonds is in the range of 8–32 kJ/mole [Sirvö 2008]. In comparison, the bond energy of covalent bonds is considerably higher, in the range of 150–500 kJ/mole. As a result, reactive strength resins are highly effective at promoting paper dry strength and can be applied at lower dosage levels. Two of the most common reactive strength resins are glyoxalated polyacrylamide (GPAM) [Farley 1994] and polyamidoamine epichlorohydrin (PAE) [Espy 1994].

However, reactive strength resins have certain limitations and are not suitable for certain paper grades. First and foremost, reactive strength resins promote paper wet strength, since covalent bonds remain intact in water. High wet strength can cause difficulties in repulping and dispersibility. Excessive mechanical force, harsh chemicals, or both are required to break down high wet-strength paper. Care must be taken if wet strength is not desired. Covalent bond formation is sensitive to the environmental conditions, such as pH, alkalinity, inorganic ions, and temperature. Paper machine white water is a rather complex system that may hinder the performance of reactive strength resins. This is probably an important reason why many conflicting results have been reported regarding the performance of reactive dry-strength resins.

Most commercial nonreactive strength resins form hydrogen bonds with cellulose fibers. Examples are cationic starch and carboxymethyl cellulose. Inside the contact area between cellulose fibers are areas with direct molecular contact and areas with void space because the fiber surface is rough. Studies have shown that nonreactive strength resins contribute to additional fiber-fiber bonds, leading to increased RBA [Moeller 1966]. Nonreactive strength resins are also believed to reinforce the existing fiber-fiber bonded areas. Compared with reactive strength resins, nonreactive strength resins are applied at relatively higher doses to achieve similar levels of dry-strength increase [Garnier et al. 2004]. This observation indicates that nonreactive strength resins are not as effective as reactive strength resins to reinforce the existing fiber-fiber bonds.

The electrostatic interaction between anionic cellulose fibers and cationic strength resins has been studied to understand its contribution to paper dry strength. The impact of the cationic charge content of cationic dextran on tensile strength of bleached kraft pulp handsheets was reported [Zhang et al 2001]. Quaternary amine groups on cationic dextran only interacted with anionic cellulose surface electrostatically. When compared
at equal mass content, handsheet tensile strength was independent of the cationic charge content. This study demonstrated that electrostatic interaction alone does not contribute to paper dry strength. This finding also explained why many commercial cationic fixation resins, such as poly(dimethyl diallyl ammonium chloride) (poly-DADAC) and polyamines prepared from epichlorohydrin and dimethylamine, are not effective dry strength resins.

Besides their chemical composition, the performance of dry-strength resins depends on their average molecular weights and molecular weight distributions. Pulp fibers are porous with a broad distribution of pore sizes. Once adsorbed onto the fiber surface, polymers may migrate into those pores. Polymers with low molecular weight can enter both small and large pores, whereas polymers with high molecular weight only enter large pores. As a result, polymers with higher molecular weight have a great tendency to remain on the fiber surface to enhance interfiber bonding.

Reported laboratory results support the above molecular weight theory. Zhang et al. [2001] studied the effect of molecular weight of cationic dextrans on paper dry strength. First, polymer molecular weight affected maximum polymer adsorption capacity on cellulose fiber. A lower molecular weight led to a higher maximum adsorption capacity, because a higher percentage of polymer chains migrated inside porous cellulose fibers. Second, when cationic dextrans were added in submonolayer doses, handsheet dry strength was greater with the higher molecular weight polymer. This was presumably because more polymer molecules were concentrated on the external surfaces to promote interfiber bonding. Finally, when treating pulp suspensions with excess cationic dextrans to saturate fiber surfaces, paper strength was not sensitive to cationic dextran molecular weight.

Many polymers, such as polyethylene oxide, are poor dry-strength resins even though they possess hydrogen-bond-forming groups. This phenomenon was explained in terms of the mixing free energy between dry-strength polymers and cellulose [Zhang et al 2000]. A high negative (thermodynamically favored) mixing energy promotes the diffusion of polymer chains into cellulose surface, resulting in paper strengthening. Conversely, if the polymer and cellulose are not compatible, they do not interdiffuse. Instead, they phase-separate to form a weak interface in the fiber-fiber bonding domain.

Because cellulose is a highly hydrophilic material, good strength resins are typically hydrophilic too. Modification of strength resins with hydrophobic groups can decrease the compatibility between the polymers and cellulose, resulting in weaker paper [Zhang et al 2000]. The paper strength decreases linearly with the hydrophobic content of a resin.

7.4.5.2. Glyoxalated Polyacrylamide

Glyoxalated polyacrylamide is probably the most widely applied reactive dry-strength resin in the papermaking industry. The synthesis of GPAM was first reported in 1971 [Coscia and Williams 1971]. The product was prepared by reacting glyoxal with a cationic polyacrylamide in slightly alkaline aqueous solution and then stabilizing it under acidified conditions. Figure 7.6 shows GPAM’s chemical composition. Under storage, the reaction between glyoxal and polyacrylamide continues, resulting in the increase of product viscosity over time. GPAM products are often produced at concentrations below 15% to extend their shelf life from gelling failures.

** PLACE FIGURE 7.6 NEAR HERE **
GPAM was initially developed as a temporary wet-strength resin for bath tissue paper grades [Farley 1994]. Bath tissue makers often add GPAM in the pulp suspension before paper sheet formation. Upon drying of the treated paper sheet, GPAM is believed to form hemi-acetal covalent bonds with paper cellulose to provide paper with wet strength. Such covalent bonds are reversible in water and hydrolyze slowly over time, leading to wet-strength decrease.

The covalent bond between GPAM and cellulose makes GPAM well suited as a dry-strength resin. First, the covalent bond energy is roughly an order of magnitude higher than that of hydrogen bonds among cellulose fibers. Thus, GPAM is effective to enhance paper dry strength at low dosages. A typical GPAM application dosage is between one to three kg/metric ton (2-6 lb/ton) of dry paper. Second, GPAM-treated paper can be repulped easily and will not interrupt papermaking production. For the past two decades, GPAM application as a dry-strength resin has become increasingly popular on various paper grades, particularly for paperboard products.

The success of GPAM as a dry-strength resin is also a result of its ability to improve wet-end operating efficiency [Lu et al. 2015]. Early GPAM products were low in cationic charge density. They were developed for tissue paper grades that use pulps with a low cationic demand. During about the last decade, GPAM products with relatively high cationic charge densities have been developed for board grades which typically have a high cationic demand [Lu and Ward 2013].

These new GPAM products often demonstrate superior retention and drainage efficiency compared with conventional wet-end coagulants such as polyamines and poly(diallyldimethylammonium chloride) (poly-DADMAC). Recent studies have also shown that GPAM products with high charge density have synergistic effects with polyacrylamide-based floculants with high molecular weight and silica microparticles [Lu 2010]. For example, the application of a GPAM product with high charge density and an anionic polyacrylamide flocculant combine both dry-strength and retention programs into one wet-end chemical program.

GPAM dry-strength performance can be adversely affected by high pH and high alkalinity levels. It is generally accepted that hydroxide ions interact with aldehyde groups during hot drying and deactivate GPAM as a strength resin. Therefore, GPAM is typically not recommended when the wet-end pH is above 8.0, the alkalinity level is above 200 ppm, or both. Precipitated calcium carbonate (PCC) is one of the most popular inorganic fillers in modern papermaking, especially for printing and writing paper grades. PCC increases wet-end alkalinity level significantly, resulting in GPAM performance loss. Furthermore, GPAM is ineffective with some recycled pulp furnishes, since PCC is introduced through recycled printing and writing paper.

Lowering the wet-end pH below 6.7 enhances GPAM dry-strength performance considerably. However, achieving this pH becomes impractical if the wet-end water system contains high PCC contents or high alkalinity levels. A large amount of acid is required to dissolve PCC and neutralize alkalinity. In addition, handling large amounts of acid raises safety concerns.

Alternative approaches have been reported to enhance GPAM performance. Wet-end application of an anionic polyacrylamide (APAM) product effectively minimized the adverse effect of hydroxide ions on GPAM [Lu et al. 2016]. Paper products treated with a combination of GPAM and APAM gained significantly higher wet- and dry-strength properties than those treated with GPAM alone under high alkalinity levels.

Finally, a recent report proposed that acidic materials could be applied on the wet paper web post-sheet forming to improve GPAM performance under high alkalinity
levels [Lu et al. 2017]. Compared with wet end pH adjustment, this approach required relatively small doses of acidic material to lower wet web pH below 6.7 before the drying section.

7.4.5.3. Polyamidoamine Epichlorohydrin

Polyamidoamine epichlorohydrin is another product being applied to enhance GPAM performance [Luo et al. 2015; Rosencrance et al. 2017]. As shown in Figure 7.7, PAE is produced by reacting polyamidoamine with epichlorohydrin at an elevated temperature. PAE contains the azetidinium group, which is reactive with carboxylate groups on the cellulose fiber surface. The azetidinium content can be controlled by adjusting the feed ratio of epichlorohydrin to polyamidoamine. Higher azetidinium contents lead to higher paper wet- and dry-strength properties.

**PLACE FIGURE 7.7 NEAR HERE**

PAE resins with high azetidinium contents are designed to increase paper wet strength. However, their application as a dry-strength resin is rather limited. Unlike GPAM, wet-strength grade PAE resins impart permanent wet strength to paper. Undesired permanent wet strength may cause difficulties in broke paper repulping and sewage clogging issues.

On the other hand, wet-strength grade PAE resins can be blended with GPAM resins to increase paper dry-strength properties. The mixtures provide unique benefits over either resin alone [Underwood et al. 1997]. As discussed in the previous section, GPAM loses its dry-strength enhancing performance under certain adverse conditions, such as high pH and high alkalinity levels. The mixtures of PAE and GPAM have been found to provide paper with significantly higher dry-strength properties than did GPAM alone. Moreover, the mixtures have led to considerably lower permanent wet-strength properties compared with PAE alone.

PAE resins with low azetidinium contents were recently reported to increase paper dry-strength properties without significantly increasing paper wet-strength properties. Instead of being used alone, they were applied with another dry-strength resin, such as GPAM [Luo et al. 2015] or APAM [Allen et al. 2001]. This two-component system provided paper with higher dry-strength properties than did either strength resin alone. In addition, cationic PAE resins promoted the retention of APAM on anionic cellulose surface.

It is worth noting that treatments described in this and the previous subsection — involving the formation of covalent bonds — represent a potential way to address concerns about high-humidity performance of paper and board products. The idea is to decrease one’s reliance on just the hydrogen bonds within paper to withstand forces of compression or tension. It has been shown, for instance, that treatment of paper with citric acid, followed by heating, can greatly increase its resistance to the effects of compressive creep when exposed to cyclic humidity changes [Widsten et al. 2014]. However, there is a need for more research in this area.

7.4.5.4. Starch Products

Starch is one of the longest-used dry-strength additives for paper. Like cellulose, starch is a polymeric carbohydrate consisting of anhydroglucose units. The way these units are linked together (with the alpha conformation rather than the beta, in the case of starch) accounts for the different properties of starch versus cellulose. It is generally
accepted that starch enhances dry-strength though hydrogen-bond formation with cellulose. The function of starch is often multifold, since starch is also applied to promote sizing, retention, and drainage. For example, the combination of cationic starch and silica microparticles is a well-accepted retention program used to create small fiber floc structure and faster dewatering, which can lead to more uniform paper formation. Starch is also the primary product used to emulsify an alkylent succinic anhydride (ASA) sizing agent. Starch products added at the wet end further enhance ASA sizing performance.

Papermaking starch products are produced from different sources, such as regular corn, waxy maize, potato, tapioca, and wheat, based on their availability and economics. Corn is the major source of starch in the United States. Potato starch is more popular in Europe, because potatoes are grown specifically for starch production in many European countries. Tapioca starch is produced in many countries, such as Brazil.

Starch is a heterogeneous material consisting of two major types of polymer: amylose and amyllopectin. Amylose is a linear polymer of anhydroglucose linked together through α-D-(1–4) glucosidic bonds. Amylopectin, on the other hand, is a branched polymer containing, in addition to linear anhydroglucose units, periodic branches at the carbon-6 position.

Amylose level varies according to the type of starch source. Most starches such as regular corn, potato, tapioca, and wheat contain about 18%–28% amylose. Corn and tapioca starches are on the higher end of this range, while potato and wheat starches are on the lower end of this range. Certain types of starches, such as waxy maize, contain almost no amylose. Conversely, high-amylose corn starches may contain up to 70% amylose.

Most starch products need to be cooked thoroughly before application. Amylose molecules have the tendency to orient themselves in a parallel fashion due to their linear structure and hydrogen-bond formation among themselves. As a result, starch products are insoluble in cold water and exist in granule forms with different sizes and shapes. Upon heating above a critical temperature, hydrogen bonds among amylose chains rupture and the starch granules become highly swollen, leading to a significant viscosity increase. As heating is continued, interaction among starch molecules will weaken more and the swollen granules will release individual polymers and small polymer aggregates, resulting in decreased viscosity. As the resulting solution is cooled, its viscosity tends to rise again because underivatized amylose molecules can reassociate with each other.

Starch products are regularly added to the paper machine wet end to increase paper dry-strength properties. Those starch products typically carry cationic charges, which help them to adsorb onto anionic cellulose surfaces through electrostatic interactions. Cationic charges are introduced by reacting starch with cationic reagents that are reactive toward the starch hydroxyl groups. A common cationic reagent is 3-chloro-2-hydroxypropyltrimethylammonium chloride. The degree of this cationization reaction is defined as the degree of substitution (DS), which refers to the average number of reacted hydroxyl groups per anhydroglucose ring. Dry-strength starch products normally have a DS value below 0.05. Products with higher DS values are more suitable for retention- and drainage-related applications.

Wet-end dry strength starch products are often applied at a dosage level one order of magnitude higher than reactive strength resins such as GPAM. The typical starch dosage is above 5 kg/metric ton (10 lb/ton) of dry fiber and in some cases, it may reach 20 kg/metric ton (40 lb/ton) of dry fiber. When added at high dosage levels, cationic starches will saturate the anionic binding sites on cellulose fibers and fines, giving poor starch retention. It is a common practice for papermakers to add an anionic strength resin
to provide additional anionic binding sites. Examples of anionic strength resins are carboxymethyl cellulose [Taggart et al. 1991] and poly(acrylamide-co-acrylic acid) [Van Handel et al. 2004; Lu et al. 2015].

Papermakers also apply cooked starch products at the size press to achieve desirable strength properties [Lee et al. 2002]. Certain modified starch products are more effective at promoting paper dry strength than unmodified starch products. Among various modified starch products, oxidized starches are excellent film formers and very effective at enhancing dry strength. However, they have the disadvantage of being dispersive to wet-end fillers when paper broke is recycled. Furthermore, unretained starch molecules will end up in the effluent, where they contribute to pollution problems, such as increased oxygen demands. In comparison, cationic surface size starches are highly retained on cellulose during the broke recycling process. In addition, cationic starch molecules concentrate mostly near the surface of paper while oxidized starch molecules tend to penetrate deeply into the paper structure. Consequently, cationic starches can provide superior optical properties, such as opacity, brightness, and print gloss.

Uncooked starches can be sprayed between different plies of multi-ply paperboard products to specifically enhance plybond [Ryu and Lee 2007]. Multi-ply boards can exhibit delamination, which is the separation between two neighboring plies. Uncooked starches are applied to minimize starch migration into the paper structure. Upon drying of the paperboard, the starch gelatinizes and fills up the void space between two plies to provide the required plybond. As a result, drying temperature, web dryness at the spraying point, and the pressing point play important roles in plybond development. The objective is to gelatinize starch while minimize starch migration into the sheet. Lower web dryness at the spraying point is preferred to retard starch migration. Additionally, an intermediate drying temperature is required. A drying temperature that is too low leads to incomplete starch gelatinization, while too high of a drying temperature leads to fast web water loss, which also retards starch gelatination.

7.4.5.5. Polyvinylamine

Polyvinylamine (PVAm) is a name frequently used for copolymers of N-vinylformamide (NVF) and vinylamine (VA). Even though PVAm has been known in the academic world for many decades, commercial PVAm products only became available in the 1990s due to the successful development of commercial NVF monomer [Kröner et al. 1999; Pinschmidt 2010].

PVAm is produced from NVF in two steps. First, NVF is polymerized to produce a homopolymer. Next, polyNVF is hydrolyzed to convert formamide groups to primary amines. This hydrolysis reaction can be carried out under either acidic conditions or basic conditions at an elevated temperature. Acidic hydrolysis is the preferred route. Specific hydrolysis degree can be achieved by controlling the amount of acid being used. At the upper end of hydrolysis conversion, the resulted copolymer may contain more than 90 mole% of VA.

PolyNVF can be produced by solution polymerization, gel polymerization, and water-in-oil emulsion polymerization. Solution polymerization of NVF is the most common commercial route and uses water as the reaction medium [Schifferstadt et al. 2000]. The subsequent hydrolysis is also carried out in water. Gel polymerization is utilized to produce relatively higher-molecular-weight products that provide superior retention and drainage in comparison with solution products [Weinheim et al. 1994]. A special type of reactor, a kneader, is used to carry out the polymerization and the
subsequent hydrolysis reaction. Water-in-oil emulsion polymerization of NVF has also been proposed in the literature to produce high-molecular-weight polyNVF [Limburgerhof et al. 1991]. NVF is first dissolved in water, and the resulting solution is then emulsified with a hydrocarbon oil. The oil phase is the continuous phase. Polymerization and subsequent hydrolysis are all carried out in the emulsion.

As shown in Figure 7.8, PVAm products may contain amidine groups due to the side reaction between adjacent VA and NVF groups. This reaction is often not desired, since the resulting amidine groups negatively affect the performance of PVAm as a papermaking aid [Lu and Tan 2013]. PVAm products can be stored under acidic pH conditions to minimize excessive amidine formation.

** PLACE FIGURE 7.8 NEAR HERE **

PVAm products can be applied either as a single-component dry-strength resin or in combination with other strength resins. When applied alone, PVAm increases dry strength through hydrogen bonds between formamide and cellulose hydroxyl groups [Truppner et al. 2005]. As a result, PVAm products with lower hydrolysis degrees deliver greater paper dry strength than do PVAm products with higher hydrolysis degrees. PVAm was also shown to have synergistic effects with an anionic polymer, such as poly(acrylamide-co-acrylic acid) (anionic PAM) [Lindsay et al. 2004] and poly(NVF-co-acrylic acid) (anionic PNVF) [Truppner et al. 2005]. However, PVAm is rather expensive to produce. Therefore, studies were also carried out to apply PVAm with various types of starch products to lower the chemical cost [Sutman et al. 2011].

### 7.4.5.6. Anionic Polyacrylamide and Polyelectrolyte Complex

Copolymers of acrylamide and acrylic acid (APAM) were developed to manufacture paper of high dry strength but low wet strength [Reynolds 1967]. The mechanism was proposed to involve hydrogen-bond formation between APAM carboxyl and cellulose hydroxyl groups. Although in theory acrylamide and hydroxyl groups can also form hydrogen bonds, such bonds do not provide a noticeable dry-strength increase. The optimal molar ratio of acrylamide to acrylic acid is between 95:5 and 85:15. In contrast, cationic polyacrylamide products are rarely used in the paper mills for dry-strength purposes. Some reports have proposed potential ester covalent-bond formation between carboxyl and hydroxyl groups at the paper machine drying section. However, the formation of such covalent bonds has been demonstrated to occur only at an elevated temperature over 150°C, which is well above paper’s drying temperature. In addition, the lack of covalent bond formation is also supported by the fact that APAM-treated paper possesses low wet-tensile strength.

APAM does not adsorb onto the anionic cellulose surfaces, and therefore cationic fixing aids are required to fix APAM into the final paper sheet. The earliest cationic fixing aid was alum (aluminum sulfate). Alum is an inorganic compound, and its charge density is a strong function of solution pH. At pH approximately 4.8, alum achieves the most effective ionic form for coagulation and the best fixation performance. Therefore, it is critical to apply the combination of APAM and alum at a pH value approximately 4.8 [Azorlosa 1951]. The strength action of APAM is largely lost when the pulp suspension is formed into paper at a pH value only a few points different from the optimum.

Cationic polymeric fixing aids were later proposed in conjunction with APAM to broaden the pH window of APAM application. These cationic polymers contain amine groups that possess cationic charge over a broad pH range. The most common example is
polyamine prepared from epichlorohydrin, dimethylamine, and ethylene diamine. This type of polyamine contains essentially quaternary amines, which are cationic independent of pH and can be applied at both acidic and alkaline pH conditions. In addition to polyamine, a variety of high-charge-density cationic polymers are suitable as APAM fixing aids. Examples are polyethylenimine (PEI), poly-DADAC, and PVAm. Low-wet-strength PAE resins have also been proposed as an APAM promoter to produce paper with high dry strength but minimum wet strength. These PAE products have low epichlorohydrin-to-amine ratios and deliver minimum permanent wet strength [Taggart et al. 1991].

7.4.5.7. Amphoteric Polyacrylamide

The word amphoteric means that a polymeric material has both positively and negatively charged groups. Amphoteric polyacrylamide (AMPAM) is the most widely used synthetic amphoteric polyelectrolyte for the paper industry. The product can be produced by copolymerizing acrylamide, a cationic monomer, and an anionic monomer in a common solvent such as water. Common anionic monomers include acrylic acid, methacrylic acid, and itaconic acid. The anionic charge of carboxylic acid depends on pH, and higher pH results in higher anionic charge density. Cationic monomers can be either a quaternary amine or a lower amine. The cationic charge of lower amines is a function of pH and lower pH results in higher cationic charge density. Quaternary amine monomers, the charge of which does not depend on pH, include DADMAC, acryloyloxyethyltrimethylammonium chloride, and methacrylamidopropyltrimethylammonium chloride. Lower amine monomers include dimethyleninopropylacrylamide.

AMPAM has a unique charge property due to the presence of both charges. At extreme acidic conditions, the product is net cationic. Increasing pH converts carboxylic acids to carboxylate ions, and the product becomes less cationic or more anionic. If the product contains only a lower-amine monomer, then it will eventually become completely anionic at extreme basic conditions, because lower amines become protonated and lose their cationic charge. There will be an isoelectric region at an intermediate pH, which depends on details of the composition. If the product contains quaternary amine monomer, it may have an isoelectric region and becomes anionic at extreme basic conditions if it contains an equal or higher molar amount of anionic monomer than the cationic monomer. However, if the product contains a lower molar amount of anionic monomer than quaternary amine monomer, then it will simply become less cationic under basic conditions.

Early AMPAM products were developed to broaden the pH operating window of anionic PAM when alum was used as a fixing aid [Schuller et al. 1959]. Only a small amount of cationic monomer was introduced to the polymer structure, and the product had a net anionic charge under neutral pH conditions. One example illustrated the dry-strength performance of an amphoteric terpolymer prepared from acrylamide and acrylic acid in a 95:5 molar ratio plus 1% DADMAC based on the weight of the mixture in comparison with a copolymer of acrylamide and acrylic acid in a 95:5 molar ratio. The introduction of only 1% DADMAC extended optimum pH from approximately 4.5 to a broader range of 5.0–9.0.

AMPAM containing a high cationic monomer content was later developed and delivered several benefits over AMPAM with a low cationic monomer content [Kawakami et al. 1981]. The molar content of cationic monomer in those new AMPAM is either equal to or higher than the molar content of anionic monomer. As a result, they
possess either cationic or neutral charge around neutral pH conditions and can retain on anionic cellulose surface without a cationic fixing aid. Furthermore, many reports claimed that the new AMPAM improved pulp retention and drainage efficiency without causing excessive flocculation and poor sheet formation.

The optimal paper dry strength was found near AMPAM’s pH with a minimum net charge [Silva et al. 2015]. The change of the polymer charge balance with pH affected how AMPAM aggregates. Under extreme acidic conditions, AMPAM is fully water soluble. AMPAM forms large aggregates under pH conditions corresponding to a balanced charge. Once retained into paper, such large aggregates are more effective to increase paper strength.

7.4.5.8. Carboxymethyl Cellulose

Carboxymethyl cellulose is produced from cellulose and monochloroacetic acid in the presence of sodium hydroxide. The function of sodium hydroxide is to convert cellulose to alkali cellulose, which is accessible and reactive toward monochloroacetic acid. The reaction introduces carboxymethyl groups along the cellulose chain and makes the hydration of the molecule possible. Because each anhydroglucose unit has three hydroxyl groups, CMC has a maximum DS of three. The common DS range of commercial CMC products is between 0.5 and 1.5.

CMC has long been known to be an effective paper dry-strength resin. CMC contains both hydroxyl and carboxyl groups, which can form hydrogen bonds with cellulose and contribute to paper dry-strength increase. However, CMC is anionic and requires a cationic fixing aid to retain on anionic cellulose fiber surfaces when added at the wet end.

One of the most common cationic fixing aids for CMC is cationic starch [Olof and Agneta 1987; Taggart et al. 1991]. As described in previous sections, high starch dosages are often required to achieve desired bonding strength increases. However, starch retention is often incomplete, causing paper machine operating difficulties such as increased BOD. At a dosage level of 5 kg/metric ton (10 lb/ton), starch retention in the sheet was only 60% [Taggart et al. 1991]. Higher starch addition levels led to lower starch retention percentages. At 15 kg/metric ton (30 lb/ton), starch retention was only approximately 44%. In comparison, the addition of CMC increased both starch retention percentage and paper dry strength considerably. The optimal dry strength was observed when CMC was added to the pulp separately after starch addition. With only 1.5 kg/metric ton (3 lb/ton) of CMC being added after the addition of 15 kg/metric ton (30 lb/ton) of starch, starch retention increased to approximately 68%. Meanwhile, paper tensile strength increased by around 12% and paper burst strength increased by approximately 28%. Furthermore, the performance of CMC depended on both the CMC dosage level and the addition sequence between CMC and starch. Adding CMC before starch or premixing CMC and starch led to lower paper dry strength.

It was reported that PVAm and CMC combinations provided higher paper dry strength than PVAm alone [Garnier et al. 2004]. Similar to the cationic starch plus CMC system, paper strength increase depended on polymer addition order and polymer addition ratio. Adding PVAm and CMC separately provided significantly higher paper strength than did premixing those two polymers. Adding CMC first also led to slightly higher strength than did adding PVAm first. Finally, at a constant dosage level and a constant addition order with CMC being added first, peak strength properties were attained at the intermediate PVAm:CMC ratio between 5:1 and 2:1. Related results were
reported by Lofton et al. [2005] and Heermann et al. [2006] for systems comprising CMC and poly-DADMAC.

Other cationic polymers have also been proposed as CMC fixing aids. Examples are PEI [Smith and Bushman 2001; Buwono et al. 2013] and PAE resins with low azetidinium contents [Taggart et al. 1991].

7.5. NONCONVENTIONAL STRATEGIES TO INCREASE PAPER STRENGTH

This section highlights some strategies to enhance paper strength that, although they are of great interest, represent recent developments or are not yet well implemented in industrial production. The term “nonconventional” is used here to cover paper strength strategies related to enzyme treatments, nanocellulose applications, and such innovations as filler agglomeration.

7.5.1. Enzymes

Enzymes can be defined as relatively large protein structures that have the ability to catalyze various chemical reactions. Enzyme use in the pulp and paper industry had been proposed over 50 years ago [Walter and Gallatin 1962]. Early studies suggested that either live fungal cells or their associated enzymes could be applied in diverse papermaking applications [Várnai et al. 2014].

Major efforts supported by governments and industries are in progress to find ways to convert wood and other lignocellulosic biomass into fuels and other usable chemicals [Wang et al. 2012]. The intent of lignocellulosic biorefineries is to fully deconstruct wood fibers to glucose (or other subunits of cellulose). In contrast, by carefully selecting enzymes and conditions, it is possible to limit the impacts on a fiber. This supports fiber modification rather than fiber degradation. Generally, the proteins used in fiber modification are too large (~5 nm) to penetrate the wall of an intact fiber. Under conditions of paper production, the activity is largely limited to the outer fiber surface, pores, pit membranes, and maybe inner lumen surfaces.

There are two broad categories of cellulosases that are currently used in the treatment of fibers: the endo- and the exo-glucanases (and blends). Understanding the mechanism, mode of action, substrate specificity, and reaction kinetics of cellulosases is important when developing cellulase-based products [Lynd et al. 2002]. Different species of wood, as well as the method of pulping (chemical, semichemical or mechanical process, or recycled) have a major impact on the surface chemistry of fibers and directly impact how different cellulases will attach and act on the fiber [Wong et al. 2000; Suurnäkki et al. 2000].

Cellulolytic microorganisms produce an array of B-1,4-glucanases during growth on cellulosic substrates in nature. These include endoglucanases that attack B-1,4-glucan chains randomly and exo-glucanases, usually cellobiohydrolases, with a strong preference for acting at chain ends, as well as B-glucosidase, which mediates the cleavage of cellobiose to glucose monomers ([Figure 7.9]). Despite intensive research in recent years, a comprehensive model that can fully describe the mechanisms by which cellulases depolymerize cellulose has not been developed. The structural intricacies of the lignocellulosic substrates also add to the complexity of the cellulose hydrolysis phenomenon.

** PLACE FIGURE 7.9 NEAR HERE **
Numerous attempts have been made to identify a single property of the substrate or enzyme as the primary determinant of the hydrolysis rate. However, review of the literature reveals that the hydrolysis appears to be controlled by the interactions among various factors, including papermaking process variables, enzyme-related factors, and substrate characteristics.

The process variables include temperature, pH, and interfering substances. The shear forces generated by the mixing mechanism, prolonged exposure to high temperature, or both can deactivate enzymes and reduce the reaction rate. These parameters can usually be adjusted to an optimum level to avoid, or at least limit, their adverse impacts.

The importance of the enzyme-related factors comes from the multiplicity of enzyme components. Although these individual enzymes are of different sizes and have different levels of activity and affinity for crystalline and amorphous regions of cellulose, they are all necessary to generate the synergistic effects required for complete hydrolysis. Inhibition of enzymes due to the accumulation of cellobiose is an example of an important, but not the primary, rate-limiting factor of cellulose enzymatic hydrolysis [Karan et al. 2012]. The non-specific binding of enzymes to lignin can also reduce the activity of enzymes and the rate at which they hydrolyze cellulose.

Numerous studies have shown that the rate and extent of hydrolysis are influenced by the properties of the substrate characteristics at three different levels: microfibril (e.g., crystallinity and degree of polymerization), fibril (e.g., lignin content and distribution), and fiber (pore size and distribution, available surface area, and degree of swelling). The cellulase anatomy and underlying amino acid composition ultimately determine how they are influenced by and interact with substrate and environment, as depicted in Figure 7.10.

** PLACE FIGURE 7.10 NEAR HERE **

In addition to wood species and fiber chemical composition, the mechanical refining of the fiber after enzymatic treatment is another very important aspect of most enzyme treatments [Garcia et al. 2002]. Once cellulases are introduced into a slurry of fibers, they immediately initiate partial cellulose hydrolysis on the surface of the fiber. Consequently, the fiber responds more readily to mechanical refining, and this results in faster fiber collapse and fibrillation. This in turn generates increased surface area, improving the ability to hydrogen bond, and thus is correlated to sheet strength properties.

The development of fibers is shown in Figure 7.11. Optimizing enzyme treatment and mechanical refining is critical to achieving the appropriate return on investment when applying enzymes for fiber modification [Fardim and Duràn 2003].

** PLACE FIGURE 7.11 NEAR HERE **

Mechanical refining of pulp fibers entails more than simply grinding them. When significant energy is required to develop sheet strength properties, there may be significant cutting of the fibers. This will decrease the average fiber length and thereby reduce sheet strength properties. Mechanical refining can also result in the formation of fragments (fines), which will hinder the draining of water from the fiber web and slow down production. The specific refiner plates, refiner plate wear, energy applied, amount
of recirculation, and many other factors impact the correct development of the fiber for the characteristics required for each grade of paper [Gharekhani et al. 2015].

Enzymatic treatment of fibers is rather simple on a laboratory scale. However, accomplishing a successful application on the paper machine is not. It requires detailed understanding of the interactions among fibers, the enzyme’s activity, the characteristics of the system, and the operation of the paper machine.

The application of cellulolytic enzymes in pulp and paper, while being a fairly new technology, has become significantly more common because of increased levels of application knowledge gained in the past number of years. As more research effort is put into the technology and new enzymes become commercially available, enzymatic applications will likely move beyond surface hydrolysis. This could include changes in charge density on the fiber surface, fiber functionalization, and deeper integration with traditional chemistries. Lastly, enzymes are being applied at relatively low levels when compared with conventional paper dry-strength resins. However, there will be a continued search for new chemistries that can act as adjuvants to improve enzyme activity or that will expand the range of conditions enzymes can tolerate. Recently, there is also a trend to derive enzymes from extremophiles that will push the boundaries of enzymes to work in areas of the pulp and paper machines that have traditionally been off limits under high pH and temperature conditions.

7.5.2. Nanocellulose and Paper Strength

The topic of nanocellulose, as well as the closely related topic of microfibrillated cellulose, has been well described elsewhere [Lavoine et al. 2012; Brodin et al. 2014; Boufi et al. 2016]. It makes sense that highly fibrillated cellulose material — commonly known as nanofibrillated/microfibrillated cellulose (MNFC) — can contribute to the development of bonding between fiber surfaces.

There are several challenges that need be addressed before MNFC technology can become widespread in the paper industry as a strength-development tool. These include a high energy requirement to prepare MNFC, difficulty of retaining MNFC during paper forming, slower dewatering rates when MNFC is added at the wet end, and ensuring the final dimensional stability of the produced paper in situations where MNFC is not retained uniformly in the thickness direction of the sheet.

Although the energy required to product MNFC can be high, an economic analysis suggests that the cost of the cellulosic material will still represent the largest cost component of the nanocellulose [de Assis et al. 2017]. Furthermore, there is potential to reduce the energy requirements for production of MNFC by application of treatments such as cellulase or certain oxidizing agents. [Pääkkö et al. 2007; Delgado-Aguilar et al. 2015].

Evidence that MNFC addition at the wet end can increase paper strength has been provided in multiple studies. [González et al. 2012; Sehaqui et al. 2013; Delgado-Aguilar et al. 2015]. Retention aids have been shown to play an important potential role in such systems [Taipale et al. 2010; Merayo et al. 2017]. The greatest strengthening effects generally have been observed when the main furnish has relatively low bonding ability, either due to low levels of refining, or in the case of recycled fibers [Sehaqui et al. 2013; Osong et al. 2014].

Promising strength effects were observed when MNFC was mixed with cationic starch before addition to the fibers [Rice et al. 2018; Hubbe 2019]. The high surface area of the MNFC makes it possible to retain relatively high levels of cationic starch, and the
MNFC structure allows the strength additive to span relatively large spaces between fibers in the paper. By use of cationic-starch-treated MNFC, in combination with a large reduction in refining energy applied to the main pulp furnish, it was possible to achieve a more bulky sheet of paper while maintaining strength properties, especially stiffness [Rice et al. 2018]. Results from the cited work, shown in Fig. 7.12, indicate that the cationic-starch-treated MNFC was highly effective for increasing the stiffness, even in the case of unrefined kraft pulp. Also, application of colloidal silica to the starch-MNFC material was found to be effective for enhancing dewatering without interfering with the strength effects.

7.5.3. Filler Agglomeration and Related Strategies

Often the delivered cost of mineral products such as calcium carbonate filler is lower than that of the fiber being used at a paper mill; such situations provide a continual motivation to increase the filler content. However, such increases in filler can be constrained by losses in paper strength. Filler particles located between fibers in the paper tend to interrupt some of the opportunities for interfiber bonding [Bøhmer 1981; Li et al. 2002].

Recently, as a strategy to decrease filler’s adverse effect on paper strength, there has been renewed emphasis on a technology that can be called filler agglomeration [Gerischer et al. 1996; Sang et al. 2012; Hubbe and Gill 2016; Song et al. 2018]. The rationale for such technology is that, by agglomerating filler particles together as bunches, there is a decrease in their effective surface area, and that translates into less interference with interfiber bonding. Fuente et al. [2005] observed that the mechanism by which cationic polymers bring about agglomeration may change as a function of their dosage; low treatments with PEI induced bridging flocculation, whereas higher dosages brought about agglomeration by charge neutralization. Paananen and Käyhkö [2013] demonstrated a system for continuous agglomerative pretreatment of filler with cationic polymer using a modern flash-mixing and injector system. Although the light-scattering ability of the filler was decreased by such treatment, it was possible to maintain the strength of the paper at a higher filler content.

Lumen loading and cell-wall-filling technologies are worthy of note as some of the most effective, but also some of the most technologically challenging, strategies to retain filler within paper without harming interfiber bonding [Middleton and Scallan 1985; Kumar et al. 2011]. By placing the filler exclusively in the insides of fibers, at least in theory, the outer surfaces of the fibers retain their full bonding abilities. Although such effects can be achieved in the laboratory, the technology has yet to be shown as economically attractive.

Literature Cited


Figure 7.1. Alteration of the breaking length of the paper sheet drying at the temperatures of 80°C, 100°C, and 120°C during eightfold recycling (replotted data) [Cabalova et al. 2011].
Figure 7.2. Sulfur concentration increase in the white water of handsheets at 73%, 87%, and 100% closure. Aluminum concentration at 100% closure is shown for comparison (replotted data) [Vendries and Pfromm 1998].
Figure 7.3. A hypothetical load-displacement curve for a paper tensile test.
Figure 7.4. Taber bending stiffness tester.
Figure 7.5. Edgewise compressive strength tests.
Figure 7.6. Chemical composition of glyoxalated polyacrylamide (GPAM).
Figure 7.7. Reaction mechanism of polyamidoamine epichlorohydrin (PAE).
Figure 7.8. Chemical composition of polyvinylamine (PVAm).
Figure 7.9. Mechanisms that cellulase components cleave the b-1,4-D-glycosidic linkages in cellulose. (Courtesy of Novozymes.)

<table>
<thead>
<tr>
<th>Cellulase Component</th>
<th>Role during Hydrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Endoglucanases (aka endo-celulase, EG)</td>
<td>Preference for amorphous cellulose</td>
</tr>
<tr>
<td></td>
<td>Makes cuts within the cellulose chain</td>
</tr>
<tr>
<td></td>
<td>Generates new cellulose chain ends for exo-cellulase activity</td>
</tr>
<tr>
<td>Exoglucanases (aka Cellbiohydrolase, CBH)</td>
<td>Preference for crystalline cellulose</td>
</tr>
<tr>
<td></td>
<td>Makes cuts from the ends of the cellulose chain</td>
</tr>
<tr>
<td></td>
<td>Progressively releases cellobiose</td>
</tr>
<tr>
<td>B-glucosidase (aka Cellobiase, BG)</td>
<td>Preference for cellobiose</td>
</tr>
<tr>
<td></td>
<td>Cuts the disaccharide, cellobiose, into two glucose molecules</td>
</tr>
</tbody>
</table>
The enzyme shape/charge changes with pH and temperature.

The fiber surface changes with pH, temperature, etc. and therefore influences binding.

CBDs display unique binding preferences.

**Figure 7.10.** Factors affecting binding of cellulases. (Courtesy of Esben Petr Friis.)
Figure 7.11. Photomicrographs of wood pulp fibers (500x), showing the bonding between individual fibers. The strength in a sheet of paper is created by hydrogen bonds at the point of intimate contact. In both cases the fibers were subjected to the identical level of refining energy. However, in the case of B, the fibers were treated with cellulase prior to mechanical refining. The action of the enzyme makes the fiber more responsive to the mechanical treatment, increasing the creation of fibrils on the surface, and in turn strengthening the bond between the fibers.
Figure 7.12. Paper stiffness as a function of freeness of the main fiber furnish as affected by subsequent optional treatment with nanofibrillated/microfibrillated cellulose (MNFC) alone (5%), with just a high level of cationic starch (1.5%), or with a combination of MNFC and cationic starch. Preliminary tests with the default furnish (neither MNFC nor high-cationic starch) gave results similar to the two lower curves. (Data from Rice et al. [2018] but plotted in a different way.)