

ABSTRACT

ZHANG, MIN. Preventing Strength Loss of Unbleached Kraft Fibers. (Under the direction of Dr. Martin Hubbe and Dr. Richard Venditti).

The purpose of this study was to understand the mechanism of paper strength loss that occurs when paper made from chemical pulps is recycled. In the case of unbleached softwood kraft pulp, it was found that the paper strength (tensile strength and compression strength) decreased with recycling. Traditional methods to increase the strength of recycled paper involve either adding dry strength agents to recycled fibers or refining the recycled fibers. These procedures increase the cost and energy usage. Fibers are also shortened during refining and more fines are produced, which leads to drainage problems and affects the productivity of the paper machine.

It was found that due to drying, unbleached kraft pine fibers lost cellulose viscosity, water retention value, fiber flexibility and accessible surface area, as determined by their ability to adsorb poly-DADMAC. Handsheets made from dried fibers had lower strength and lower apparent density compared to the corresponding primary handsheets made from never-dried fibers. With the increase in drying temperature of virgin fibers, the above properties of dried fibers or strength of recycled handsheets experienced larger effects, especially for drying temperatures over 150 °C.

In this research it was hypothesized that adding certain chemicals to virgin fibers before drying could prevent strength loss upon recycling. Results showed

that relatively low molecular weight additives (such as sucrose and glucose) appeared to interfere with the mechanism of pore closure during drying and improved the strength of recycled paper. Higher molecular weight chemicals (such as starch) added to never dried virgin fibers also increased the strength of the recycled paper, but this was attributed to residual chemicals being retained on the fiber surface during recycling. Although the effect of adding certain chemicals to virgin fibers before drying could significantly prevent strength loss in recycled paper, it was determined that improvements of recycled paper strength due to refining were of much larger magnitude.

It was found that recycled handsheets had lower strength compared with virgin handsheets within the pH range from 3 to 8, which encompasses the majority of papermaking applications. There was no significant effect of pH on paper strength within this range. The lack of effect of sheet forming pH on paper strength implies that under practical papermaking conditions, for the type of pulp considered in this research, adjusting sheet forming pH may not be an effective tool for increasing paper strength. The results from water retention value and cellulose viscosity measurements also supported this conclusion.

The fiber flexibility tests showed that the method is useful to determine the flexibility of individual fibers. In the case of sugar treatment, treated fibers showed higher flexibility than untreated fibers after drying, and glucose had a larger effect than sucrose. With respect to papermaking conditions, fibers were more flexible under alkaline conditions than fibers under acidic conditions, but fibers became less flexible with increasing salt concentration and hardness.

**PREVENTING STRENGTH LOSS OF UNBLEACHED
KRAFT FIBERS**

by
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BIOGRAPHY

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CHAPTER 1

Introduction

Paper recycling is an important part of the paper industry, mainly motivated by economic profitability concerns. Paper recycling also has benefits to society including the reduction of landfill loadings and less dependency on forest resources. Paper and paperboard are the largest component in the composition of municipal solid waste (MSW) and constitute a large percentage of the materials going to landfill [1]. Fibers that have undergone a manufacturing process are collected and used as the raw material (secondary fibers) for recycled paper products. With pressure on solid waste disposal systems and other environment concerns from the government and public, and with increasing industrial interest in economics and treatment process progress for secondary fiber, secondary fiber utilization is currently increasing at a rapid pace.

In the U.S., paper recovery increased from 26.8 million short tons/year (around 25% recovery rate [1]) in 1985 to 48 million short tons/year in 2000 (nearly 45% recovery rate [2]). Almost 40 million short tons/year are recycled back into domestic paper and paperboard production [3]. In other words, 36.5% of the pulp fiber comes from recycled waste paper in 1999. This is up from 25% in 1988 [2]. In many other countries wastepaper is an even more important resource, especially for countries with a scarcity of forest resources. However, in addition to bringing contaminants such as ink, wax, grit *etc.* that affect the process and final product quality, wastepaper is considered to be inferior as a fiber resource relative to virgin fibers. The present work will focus on the

changes of fiber properties due to recycling and how the changes affect the properties of papers made from recycled fibers.

With increasing recycle of waste paper and paperboard, researchers have become more interested than ever in the changes of properties of fibers during recycling. It has been observed that the strength of secondary paper made from recycled chemical fibers is reduced compared with that of the initial paper, and it is also known that the properties of paper made from kraft pulp deteriorate with increasing level of recycling [4-10]. The strength loss of recycled paper limits the number of recycles of waste paper and paperboard, and it limits the usage of recycled fiber per unit production.

Compositions of Wood Fibers

Paper has traditionally been defined as a felted sheet formed on a fine screen from a water suspension of fiber [11]. Wood fiber is the main component of paper. It is known that the properties of wood fibers affect the final paper properties. Cellulose, hemicelluloses and lignin are three major components of wood fibers. These compositions change with different wood species, wood age, location, and wood morphology. The typical compositions of softwood and hardwood are shown in Table 1-1.

Table 1-1. Compositions of woods [11]				
Wood Species	Cellulose	Hemicelluloses	Lignin	Extractives
Softwood	42 ± 2%	27 ± 2%	28 ± 3%	3 ± 2%
Hardwood	45 ± 2%	30 ± 5%	20 ± 4%	5 ± 3%

Cellulose fibers exhibit a number of properties that fulfill the requirements of papermaking [11]. The major advantages of the cellulose fibers include high

tensile strength, conformability or flexibility, resistance to plastic deformation, water insolubility, hydrophilicity, inherent bonding ability, and chemical stability. The chemical formula for cellulose is $(C_6H_{10}O_5)_n$, where n is the number of repeating sugar units. The cellulose unit structure is shown in Fig. 1-1.

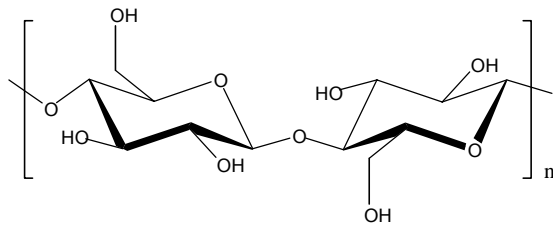


Fig. 1-1. Cellulose structure

The actual repeating unit of cellulose is cellobiose, two glucose molecules linked through a β -(1,4) linkage. The degree of polymerization (DP) value (weighted averages) for wood fibers is about 600-1500 [11].

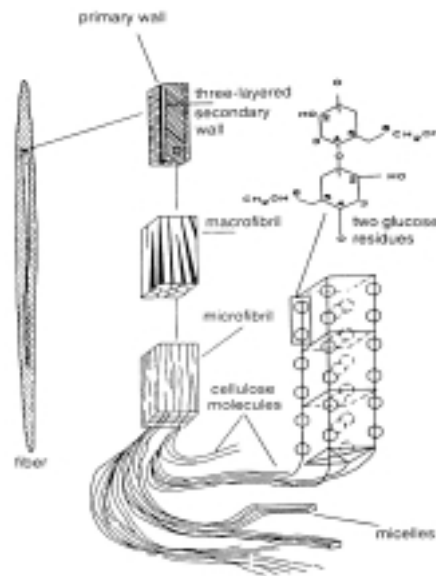


Fig. 1-2. Microscopic and submicroscopic structure of cellulose [11]

As shown in Fig. 1-2, cellulose in wood fibers is organized as cellulose microfibrils, where amorphous and crystalline regions are found. Since the solvent or reagents can more easily access amorphous regions, cellulose

degradation is more likely there. Decreasing the DP of cellulose below a certain value will destroy cellulose strength [11], which in turn reduces paper strength.

In contrast to cellulose, hemicelluloses have side linkages, which make them more easily degraded and dissolved in water compared to cellulose. At the same time, with short branching chains, hemicelluloses can resist the development of crystallinity that has been proposed to happen during drying of cellulose [12]. In softwood the main hemicellulose is galactoglucomannan (20%) as shown in Fig. 1-3, and the minor is arabinoglucuronoxylan (5-10%) [13]. In hardwood the main hemicellulose is glucuronoxylan (15-30%), as shown in Fig. 1-4, and the minor is glucomannan (2-5%). It is noted that the carboxylic groups in some hemicelluloses can benefit fiber swelling and improve the relative bonded area between fibers during paper formation.

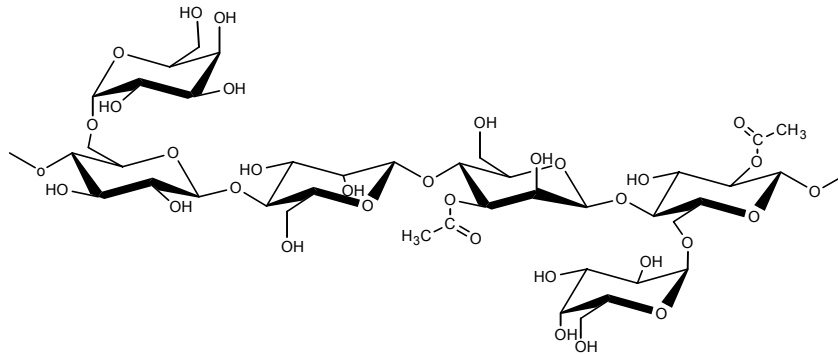


Fig. 1-3. Galactoglucomannan structure in softwood

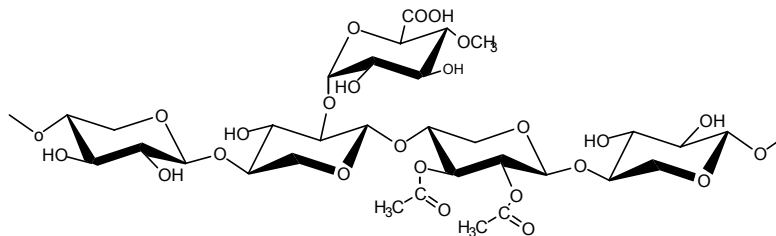


Fig. 1-4. Glucuronoxylan structure in hardwood

Second to cellulose, lignin is among the most abundant biopolymers on earth. The structure of lignin is very complicated. Chemically, lignin is built from phenyl propane units linked together by different bonds, as shown in Fig. 1-5. Lignin is considered to be a three-dimensional network that restrains the swelling of the cell wall of the fiber. The less swollen fibers reduce the fiber-fiber bonding during sheet forming and therefore weaken paper strength. For applications such as newsprint in which permanence is not that important, mechanical pulping is used to retain the lignin and to maintain a high pulping yield. However, in most cases where strength and permanence of the paper are important, papermakers want to remove lignin from fibers using as much as possible during pulping and bleaching. Since lignin holds cellulose and hemicelluloses together in the fiber wall, it is expected that lignin cannot be completely removed without damaging cellulose and hemicelluloses.

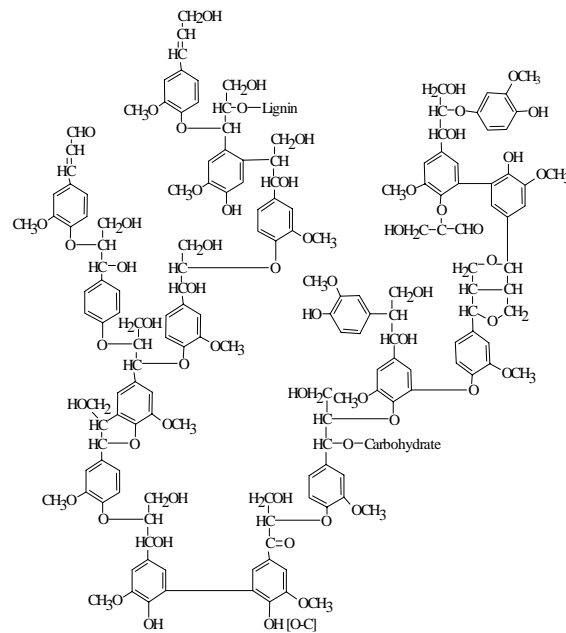


Fig. 1-5. Lignin structure [14]

Cell Wall Structure of Wood Fibers

A fiber consists of three main layers, the middle lamella (ML), the primary wall (P), and the secondary wall. Figure 1-6 shows the simplified structure of wood fiber cell wall. There are three sub-layers in the secondary wall, a thin outer layer (S_1), a thick middle layer (S_2), and a thin inner layer (S_3) towards the lumen (L). In all conifers and in some hardwoods there is one more layer, the warty layer (W), which is located on the inner surface of the cell wall adjacent to the S_3 layer, not shown in Figure 1-6 [13]. The Middle lamella is located between the fibers and works as glue to bind the fibers together. In both hardwood and softwood fibers, the lignin concentration is high in the middle lamella and in the primary wall, especially in the cell wall corners.

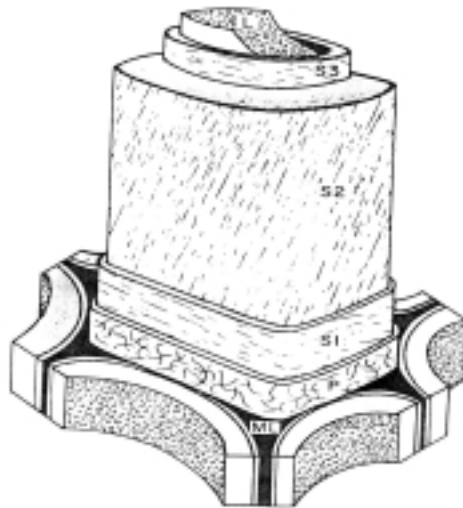


Fig. 1-6. Diagram of a cell wall [11]

The main purpose of pulping is to release fibers from the wood. In other words, pulping separates fibers that are bonded together through the middle lamella. Wood fiber can be separated either by mechanical methods, chemical methods or a combination of both. Chemical pulping is a process in which the lignin in the secondary wall is also removed in addition to the lignin in the lamella.

Unlike in the middle lamellar layer, the lignin concentration is low in the secondary wall, but at least 70% of lignin in softwood is located in the secondary wall due to its thickness. Since lignin is embedded in the fiber with cellulose and hemicelluloses together, removing lignin leads to a loss of yield and lower fiber strength, which is due in part to the removal or the degradation of carbohydrates. Figure 1-7 shows how lignin, cellulose and hemicelluloses are distributed in the secondary wall according to a widely accepted model [15].

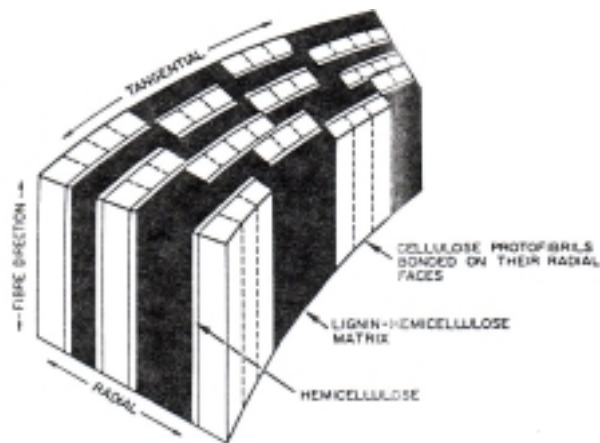


Fig. 1-7. Schematic of the proposed lamella model for ultra-structural arrangement of lignin and carbohydrate in the secondary cell wall [15]

As described above, cellulose dominates fiber strength and hemicelluloses can improve fiber swelling. In order to achieve high paper strength, papermakers want to avoid the degradation of cellulose and hemicelluloses during pulping. One of the consequences of chemical pulping is the formation of relatively large pore sizes as shown in Fig. 1-8. The pore size distribution in mechanical pulp fibers is dominated by 1 nm pores [16]. By contrast, kraft and bleached kraft fibers have a majority of 5-20 nm diameter pores [17]. It has been said that the pore size increase is due to removed lignin and hemicelluloses from cell walls during pulping and bleaching. Fibers become more swollen in water due to the

removal of lignin from the cell wall. The significant difference between chemical pulps and mechanical pulps is that mechanical pulps have high yield and keep much more lignin in the fibers. Due to this difference, properties of fibers show different responses with respect to drying. Mechanical pulps were found to have less hornification, which is defined as the shrinkage of fibers and formation of irreversible hydrogen bonds during drying. By contrast, chemical pulps are relatively susceptible to hornification. The changes of fiber properties are assumed to dominate the strength properties of secondary paper made from recycled fibers.

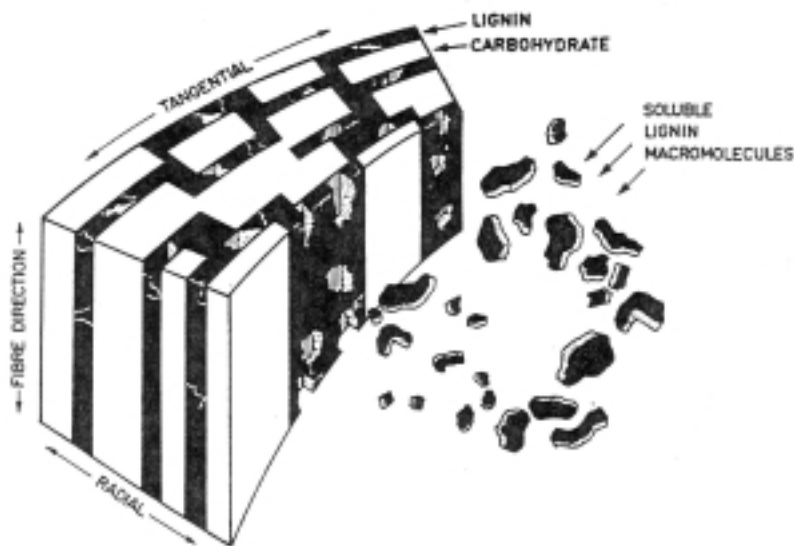


Fig. 1-8. Schematic of the breakdown and solution of lignin during chemical pulping [15]

Theories of Paper Strength

It is necessary to know the failure mechanisms of paper in order to understand the effect of recycling on paper strength. In cases where the nature of the strength test is not specified, usually the word “strength” is assumed to mean tensile strength, a property that is of primary concern to papermakers.

It was said that paper strength is governed by the failure of the inter-fiber bonds and also by fiber rupture in well-bonded papers [18]. These two failure modes are difficult to separate, because papermaking operations affect both the properties of fiber-fiber bonds and the structure of sheets. There are many microscopic models of paper strength involving the competition between bond and fiber failures [19-21]. Page derived his model [20] for tensile strength starting from the experimental observation that tensile strength is proportional to the fraction of broken fibers along the rupture line of paper. The following equation for tensile strength is known as the Page Equation:

$$\frac{1}{T} = \frac{9}{8Z} + \frac{3w_f}{\tau_b l_f RBA}$$

where:

T = tensile strength

Z = zero span strength of paper (reflecting fiber strength)

w_f = fiber width

l_f = fiber length

τ_b = the breaking stress of bonds (breaking force over bonded area)

RBA = relative bonded area

The Page model is different from the Shallhorn-Karnis model that presents the same predictions, except that the paper strength is proportional to the fiber width in the Shallhorn-Karnis model [21]. From the Page Equation, in those cases in which paper strength is limited by the fiber bonding term, it is easily concluded that the inverse of tensile strength is linearly proportional to the

inverse of fiber strength, fiber length and relative bonded area (RBA). A change in any of these factors will affect the tensile strength. Since the zero span strength and fiber length are already fixed after fibers are delivered to paper mills from pulping mills, increasing tensile strength is focused on bonded area and bond strength. Adding dry strength agents or extending refining is a common practical approach to gain strength. In such cases the increased strength has been attributed to the increased RBA or the improved bond strength [22].

Unbleached kraft pulp is a major component of furnish for linerboard products. One of the main uses of linerboard is in the production of corrugated containers that protect contents from compression forces during packing, storage and distribution. Although tensile strength is the most important property in some grades, corrugated containers seldom fail in a tensile mode. Rather, compression strength of the linerboard is a much better predictor of failure. With stack heights constantly increasing in modern warehouses and pallets, the compression strength of corrugated boxes, always a matter of concern, is becoming more important to converters and end users.

Though compression strength is of great concern to the manufacturers of linerboard, relatively few studies have considered the effect of recycling on compression strength. Seth et al. [23] found that, at a low degrees of bonding, compression strength depends strongly on bonding, but that as bonding is increased, a limiting strength is reached that is independent of any further increase in bonding. They suggested that the compression strength of paper is controlled by the compression strength of fibers at higher degrees of bonding.

This behavior is similar to that of tensile strength according to the theory proposed by Page [24]. As suggested by Cavlin and Fellers [25], “failure in compression can be seen as the result of an unstable state of loading with two complementary failure mechanisms, that is, the failure is triggered either by buckling of fiber segments that was predominant in low density sheets, or by shear dislocations of fiber walls caused by flow of microfibrils that was predominant in high density sheets”. Sachs and Kuster presented evidence that the sequence of failure first starts from dislocation of the cell wall tissues [26]. An interfacial separation of the S_1 and S_2 cell wall layers leads to separation of fiber-to-fiber bonds and delamination of fiber cell walls, leading to failure of the linerboard. Buckling of fibers follows failure.

Effect of Recycling on Paper Strength

Many investigations have reported that paper strength drops after recycling in the case of chemical pulps [4-10, 27-34]. Figure 1-9 shows typical behavior of chemical pulps during recycling, based on the work of McKee [4]. In his work unbleached kraft fibers were refined with a laboratory Valley beater to 325 ml freeness, and the recycled fibers also were refined to the same freeness in each cycle. It was found that the recycled paper showed lower strength in term of breaking length, burst, fold and strength as well as apparent density. Increases in tear, stiffness, and light scattering coefficient were observed. All properties appeared to involve a greater change in the first recycle, and most properties became stable after four successive recycles. Similar behavior was found in bleached kraft pulp, presented by Howard and Bichard [7], although no additional

refining was applied in any of the recycling procedures except disintegration with a standard impeller.

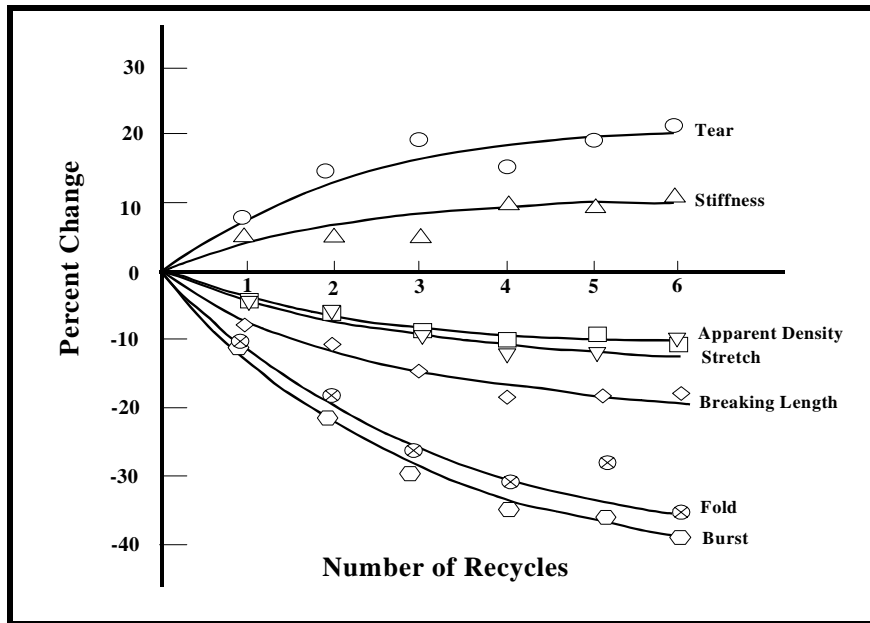


Fig. 1-9. Effect of recycling on unbleached chemical pulps [4]

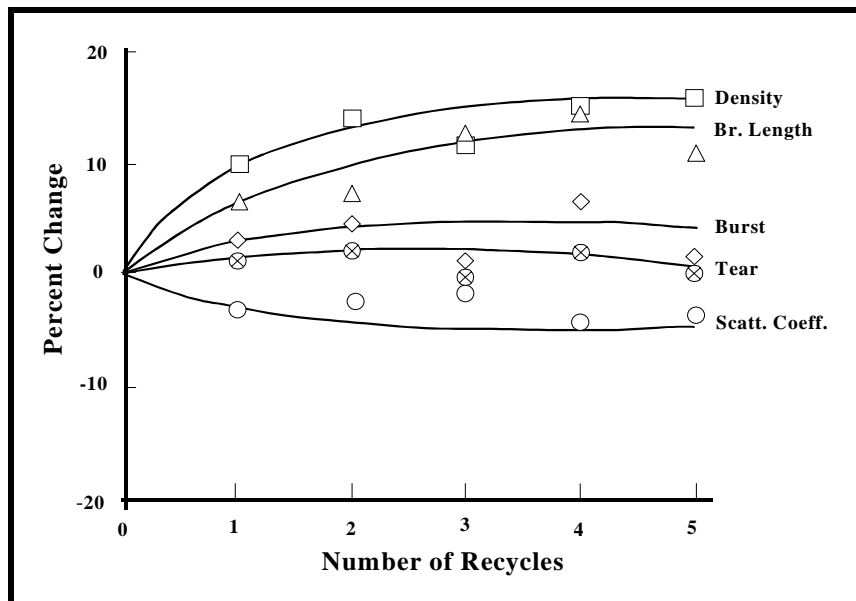


Fig. 1-10. Effect of recycling on mechanical pulps [7]

By contrast, researchers found that mechanical pulps showed completely different responses to recycling [5-7]. Figure 1-10 represents a general experience for mechanical pulps, based on the work of Howard and Bichard [7].

Increases in tensile strength, apparent density and burst were found after recycling in the cases of stone groundwood pulp (SGW) and chemithermomechanical pulp (CTMP). Reduced scattering coefficient was also observed.

The different responses to recycling between chemical and mechanical pulps indicate that lignin may play an important role during recycling. Further work conducted by Bovin *et al.* provided evidence to support such an assumption [5]. Different chemical pulps showed different responses with regard to recycling. Paper made from unbleached sulfite pulp was less affected by recycling compared to paper made from bleached pulp [5]. Low-yield pulps experienced greater loss in paper strength compared to relatively high-yield pulps during recycling [6]. It was suggested [30] that one of the reasons was that the cell walls of mechanical fibers are not extensively delaminated in the wet state; therefore, hornification is limited during drying and thus has little effect on the subsequent fiber-fiber bonding. The relatively stiff, uncollapsed fibers of mechanical pulps tend to become flatter and more flexible after each successive papermaking and reslushing cycle. These changes tend to increase the relative bonded area and form a thinner, denser sheet.

It was found that the loss of tensile strength of secondary paper due to recycling in the case of bleached sulfite spruce pulp was most pronounced when the fibers were dried at higher temperatures during the formation of primary sheets [35]. The effect of temperature on recycled paper was also confirmed by Lundberg and De Ruvo for bleached pine kraft pulp [36]. Pycraft observed that

there was an optimum drying condition for the tensile strength of primary paper made from refined bleached sulfite pulp [37]. Above the optimum drying condition, increased drying temperatures produced weak primary paper and weak recycled paper. By contrast, below the optimum drying condition, increased dryer temperatures produced strong primary paper but weak recycled paper. This observation is consistent with the finding of Brecht that the stronger primary strength, the greater will be the strength loss during recycling in the case of unbleached kraft pulp [38].

Effect of Drying on Fiber Properties

It is common to apply the Page Equation to examine the effect of recycling on tensile strength. The effect of drying during recycling on fibers is paid much attention by researchers, since fiber properties are affected greatly during drying.

It has been proposed that, in the wall of the wood fiber, water is held in a micro-porous gel of hemicelluloses and lignin [16-17, 35-36, 39]. By removing the lignin and some of the hemicelluloses by pulping, water filled the space where lignin and hemicelluloses occupied previously, resulting in an increased amount of water in the cell wall [16]. When pulp is dried from water, the fibers become less porous. It has been shown that fiber pores shrink or close, and that increased crystallization takes place at the fiber surface [35, 39-42]. The loss of micro-porosity has been mainly attributed to the Campbell effect. In other words, surface tension forces lead to the collapse of intra-fiber pores [43]. Allan and Ko suggested that the forces of attraction and repulsion between the lamellae of the cell wall are also responsible for the change of fiber pores when water is being

removed from fibers [44]. A recent study using the technique of Field-Emission Scanning Electron Microscopy (FE-SEM) indicated a distinct difference in fiber surface morphology between air-dried fibers and freeze-dried fibers [45]. Porous structure on the surface of freeze-dried fibers was observed; by contrast, tightly packed macro-fibrillar structure was visible on the surface of air-dried fibers. The observation provided direct evidence to support the claim that fiber pores collapse during drying. The main consequence of this change in fiber properties is a reduced bonding ability between the fibers. Reducing bonding has been described as irreversible hornification, which implies a stiffening or hardening of the fiber [46-49]. Scallan developed another cell wall model shown in Fig. 1-11 to explain the mechanism of hornification [50].

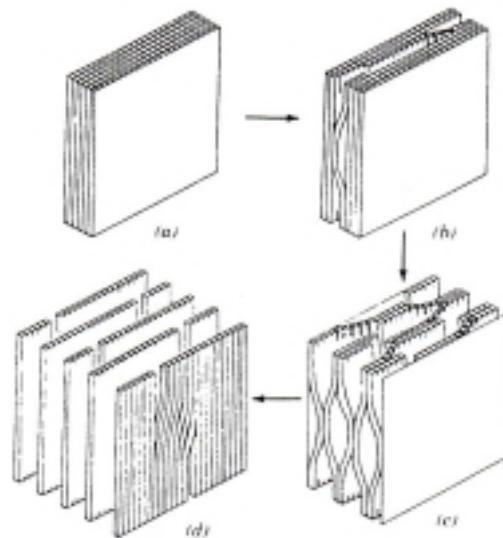


Fig. 1-11. The pattern of internal fibrillation of cell wall with progressive swelling from (a) to (d) [50]

This model is similar to the model proposed by Kerr and Goring for the ultrastructural arrangement of lignin and carbohydrate in the cell wall [15]. As shown in Fig. 1-11, phase (a) represents fibrils that are all tightly packed and totally hydrogen bonded within the dry cell wall. With progressive swelling of the

structure, bonds between fibrils are broken, leading to the patterns of internal fibrillation from phase (b) to phase (d). It was suggested that phase (c) represents the typical arrangement of microfibrils in the wood and throughout pulping. When fibers are drying, the fiber wall changes from phase (c) to phase (a). However when the dried fibers are rewetted, the fiber wall reverts only back to phase (b) due to drying. Thus, there are hydrogen bonds formed during drying that cannot be broken upon rewetting [49]. The fiber pores become small and less swollen in the final structure phase (b) compared to the condition of never-dried fibers.

The Fiber saturation point (FSP), determined by the technique of solute exclusion [17], and water retention value (WRV), determined by the technique of centrifugation [51] are two indices used to measure the internal fiber swelling capacity. The technique of WRV is more commonly used due to the simplicity of the measurement and the fact that the method provides a rapid result that has a good correlation with FSP [52]. It has been found that recycled chemical pulp has a lower WRV or FSP in comparison with the never-dried chemical pulp [7, 27-36, 48-49]. However, WRV remains almost constant in mechanical pulps after recycling [7, 33]. A possible explanation for the observed effect is that the interfibrillar spaces in the fiber wall, represented by phase (a) in Fig. 1-11, are filled not just with water, but also with ligo-hemicellulose gel [49]. It was suggested that the gel behaves reversibly during drying-rewetting cycle and prevents cellulosic surfaces from coming into direct contact during drying [53].

It has been noted that there was a considerable drop in FSP when a dissolving pulp was dried at 120 °C, compared to that dried at 25 °C [54]. Lundberg and De Ruvo found that higher temperatures during drying of papers produced less swollen fibers [36]. They reported that pulp prepared from sheets dried at higher temperature could not gain the same WRV as the corresponding virgin pulp even after prolonged beating. It was found that pores closed by drying under room temperature conditions could be opened by water treatment, but higher temperatures caused more permanent closure of the larger pores, based on results by the technique of solute exclusion [35]. In the mechanism proposed by Stone and Scallan, it was suggested that fiber pores were subject to inelastic deformation during drying, and the effect was more likely to be associated with the larger pores. It is reasonable to expect that, due to this process, the large pores would close up preferentially during drying, and high temperature would promote the change of fiber pores [35, 39].

Although recycling has significant effect on fiber pores, it was found that the effects of recycling on fiber length, coarseness and fiber perimeter were not significant at the 90% confidence limit if there was no additional refining during recycling [31]. Ackermann *et al.* also concluded that changes in fiber length, coarseness, and distribution of fiber fractions due to recycling were usually negligible without calendering and beating during recycling [33].

Effect of Recycling on Fiber Strength

According to the Page Equation, fiber strength is another important factor for final paper strength in addition to fiber morphology. Fiber strength is

represented by zero-span tensile strength. However, there have been contradictory findings for the change in fiber strength during recycling. Cilder and Howarth reported that the zero-span tensile strength decreased 13% in the first cycle and 20% after four cycles of recycling when the bleached sulfite pulp was beaten to the same freeness with a Valley beater in each cycle [55]. McKee and Horn also found a significant drop in zero-span tensile strength for unbleached kraft pulp during recycling when the pulp was beaten to same freeness in each cycle [4, 10]. By contrast, Bobalek and Chaturvedi found a slight increase for bleached kraft pulp of northern pine and a significant increase for bleached kraft pulp of aspen in zero-span strength during recycling without any further refining [9]. Similarly, Ellis and Sedlachek reported an increase in zero-span strength for bleached kraft hardwood [31]. Van Wyk and Gerischer found that zero-span tensile strength remained almost constant during recycling when a pilot paper machine was used in their research [8]. Cardwell and Alexander observed no significant change in zero-span tensile strength when the unbleached softwood kraft pulp was refined to approximately same breaking length in each cycle [56]. Without additional refining during recycling, Howard and Bichard found no significant change in fiber strength upon recycling for all kinds of pulps [7]. They concluded that there was no fundamental reason that a drying-re-slushing cycle should change the fiber strength. They suggested that papermaking or recycling processes might affect the observation, due to factors such as fines loss, or fiber damage due to calendaring [32].

Postulated Mechanisms for the Strength Loss of Recycled Paper

It is generally believed that the loss of paper strength in the case of chemical pulps results from the loss of bonding, either from the loss of bonded area or from the loss of bond strength per unit of bonded area. Ellis and Sedlachek [31] considered the case of recycled fibers that had not been further refined and concluded that the fiber-fiber bond strength per unit area of bonding was the same as in the case of virgin fibers. This implies that the relative weakness of the recycled paper sheet is due largely to the inability of the fibers to develop bonded area and partly to the changes in zero-span tensile strength. It is generally agreed that the changes of fiber morphology and topography upon drying are a main cause for the loss of bonding area. Fibers experience hornification and become stiffer.

Brecht [38, 57] thought that losses of fines are responsible for strength loss. Thode and Ingmanson [58-59] indicated that fines could have less bonding capability than swollen fibers on a unit area basis. A study from Cardwell and Alexander [56] showed that fines are less important when attempting to regain a given breaking length than they are when trying to replicate a given freeness after successive recycling.

Prior Studies to Improve the Strength of Recycled Paper

Previous work to overcome strength deficiencies of recycled kraft fibers has focused on ways to increase the bonding ability of fibers after they already have been recycled.

One approach is to apply additional refining. The purpose of refining is to improve fiber bonding potential by regaining the fiber swelling that was lost during recycling. It was found that refining could increase the recycled paper strength [60]. It is unclear whether the original hornification is removed by refining or the recovery of swelling ability results from new changes in the fiber wall [33]. It has been shown that mechanical beating can restore the swelling capability of hornified fibers [49, 61], as it can do for virgin fibers, improving fiber swelling and paper strength [35]. Some researchers have disagreed that hornification can be reversed by beating; they based this conclusion on the idea that hornification is caused by crystallization [62-63] and that beating cannot alter the degree of crystallinity of fibers [64-65]. Stone and Scallan found that beating could improve the degree of swelling of dried chemical pulp to and even beyond the level of the never dried pulp [39]. However, refining recycled pulp tends to shorten the fibers and to produce extra fines. The fines make the furnish more difficult to drain and can impair the paper machine output. Szwarcstajn and Przybysz concluded that original chemical fiber fines can lose their contribution to bond strength upon hornification and cannot be reversed by beating [65]. The authors suggested that adding refined virgin pulp to recycled pulp can improve recycled paper strength disproportionately. It was proposed that refined virgin pulp contains both active fibers and active fines [66]. De Ruvo and Htun found that recycled fines showed less swelling compared to virgin fiber fines, and concluded that recycled fines behaved more like fillers with less effect on the strength and more effect on the drainage [60]. By contrast, Laivins and Scallan

paid much attention on the pulp swelling without considering paper strength. They showed that the swelling ability of recycled fines and recycled fibers could be recovered through modest beating for chemical pulps [67]. Weise attributed the difference to measurement methods and drying conditions [12].

Another approach is to add dry strength agents to the recycled fiber to increase the bonded area or the strength per unit area of bonds between adjacent fibers [68], the same technique applied to virgin pulps for upgrading primary paper strength [22, 29, 69-72]. Starch derivatives are the most common dry strength additives for improving recycled paper strength [69]. In addition to starches, polyacrylamide products (PAM) [73] and guar gums [74] are also used in the paper industry. Two main mechanisms are involved in the strength development from dry strength additives [69]. In the case of starch, the first involves the improvement of sheet formation. The second involves the formation of extra hydrogen bonds between its free glucose hydroxyl groups and fiber surface cellulose molecules to enhance fiber-fiber bonding. It was concluded that dry strength agents, such as cationic starch, contributed to the increase in bond strength per unit of bonded area more than the increase in bonded area [22, 75-76].

Other approaches are to subject the fibers to increased pH [77-82], increased wet pressing pressure [5, 55] or conditions that favor rehydration [83].

Sodium hydroxide has been used in wastepaper since 1800 to help ink removal or the disintegration of sized paper [32]. It is noted that the treatment of recycled fibers with sodium hydroxide improved the tensile strength of secondary

paper [77-82]. It was found that fibers became more swollen due to treatment with sodium hydroxide when dealing with unbleached pulps [82]. Two theories were proposed for the effect, both related to the dissociation of acidic groups. One is based on electrostatic repulsion. With the increase of pH value, the degree of dissociation of carboxyl groups increases, which increases the repulsive force between microfibrils [84-85]. The fibers swell with water and are more flexible due to this. The other is related to the Donnan equilibrium [86]. The swelling of cellulose gel is considered to be caused by an osmotic pressure differential resulting from a difference in concentration of mobile ions between the interior of the gel and exterior solution. It was found [87-89] that the difference in the concentration of mobile ions within the wall and outside of the wall increased initially, reached a maximum, and then decreased with the increase of pH values.

It was found that increasing wet pressing pressure during the formation of recycled paper could improve the paper strength; however, pressing cannot completely recover strength loss due to recycling [5, 38]. It was also confirmed by our unpublished data that the effect of drying on the paper strength could not be removed through increasing wet pressing pressure alone, without other processes such as refining or adding dry strength agents, Appendix 1.

It was observed that strength properties of recycled paper were improved after the treatment of oxygen delignification in old corrugated container (OCC) pulp [90] and ozone treatment in old newspaper (ONP) pulp [91]. It was also found that fibers became more swollen after the treatments. A possible

explanation is that more cellulose in the fiber wall was exposed, resulting from lignin removal with the treatments.

Fractionation was suggested as another option when the waste raw material contains large proportions of different fiber types [32]. Long fibers and short fibers were separated followed by different procedures to obtain desired paper strength with efficient use of energy.

Since there is good evidence that the loss of paper strength is related to fiber hornification, it is desirable to prevent the process during the making of the primary paper products. As described earlier, it is proposed that hornification is associated with the formation of irreversible hydrogen bonds. Hydroxyl groups in the cellulose chain are mainly responsible for the formation of hydrogen bonds.

One approach is related to substitution of the hydroxyl groups with other groups that can interfere with the formation of irreversible hydrogen bonds. It was found that the substitution of hydroxyl groups of virgin pulps with carboxylic acid groups through carboxymethylation or with methoxy groups through methylation could improve the swelling of recycled fibers and prevent hornification [49, 85]. It was observed that with pulps containing carboxyl groups, the degree of hornification during drying was not decreased significantly if the pulps were dried with the acidic groups in their hydrogen form instead of in their ionized form (e.g. in the presence of Na^+) [85]. It is proposed that carboxymethyl groups in the hydrogen form have same capability of forming hydrogen bonds as the original hydroxyl groups, and in sodium form produce osmotic pressure that disrupts the formation of additional cross-links during drying. Results from

Williams *et al.* provided indirect evidence to support such an explanation [92-93]. When the paper made under alkaline condition was dispersed, the recycled fibers could form relatively strong recycled paper in the term of fold endurance. In the case of the methoxy group, it was found that this group need not be in an ionized form to prevent hornification, because it is incapable of forming hydrogen bonds [49]. However, no data was reported about the effect on the strength properties of recycled paper in these two cases. A recent study by Gruber and Johann demonstrated that the modification of virgin softwood sulfite fibers by the introduction of spacer groups, derivatives obtained through the reaction of α , β -unsaturated substances or amino derivatives with the cellulose, resulted in less hornification and increased the strength properties of recycled paper [94].

Another approach is to add chemicals to the never-dried fibers before the first cycle of sheet forming [95]. Such additives can form hydrogen bonds with hydroxyl groups and obstruct the bond formation between cellulose microfibrils within the fiber during drying. It was observed that glycerol and sucrose addition to never-dried unbeaten kraft pulp resulted in less loss of recycled paper strength than untreated pulps [95]. It was proposed that sucrose and glycerol could prevent the formation of irreversible hydrogen bonds between during drying by forming bonds with cellulose and that this kind of bond can be more easily broken on rewetting than the intra-fiber bonds [95]. It was suggested that there existed weak and strong hydrogen bonds in fibers [96]. The strong bonds are responsible for the irreversible bonding upon recycling. This explanation is similar to the theory proposed by Milichovsky [97]. There are two or three types

of hydrogen bonds responsible for oriented (crystalline), less oriented, and unoriented (amorphous) areas in native cellulose fibers. The ability to destroy hydrogen bonds with water depends not only on the strength, but also on the nature of the hydrogen bonds. Sodium chloride was not found to be as effective as had been expected based on an assumption that the electrolytes would interfere with the formation of hydrogen bonds [49].

Since a very high concentration (20%) of sugar treatment was required to retain full strength, such an approach may be impractical for industry. Polymeric chemicals at low concentration were considered by Higgins *et al.* [95] and Grau *et al.* [98]. Although some kinds of chemicals were found to have positive effects, it is suggested that these polymeric additives are not wholly removed from the pulp after recycling and reslushing, so that they can also function directly in the conventional way expected for dry-strength resins [95]. It was found that hornification was not prevented with addition of dry strength agents [98].

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CHAPTER 2

Objectives

As described in the previous chapter, the loss of paper strength during recycling is a critical issue for the paper industry. Although many studies have been conducted in this area to determine the mechanisms of strength loss, to prevent the loss of paper strength, or to improve recycled paper strength, researchers still are not confident of the exact mechanisms for the strength loss. For instance, the formation of intra-fiber hydrogen bonds has been claimed to be responsible for irreversible pore closure [1], which leads to the observed strength reduction of recycled paper. It was found that sucrose and glycerol at high levels could prevent the strength loss due to recycling. It was proposed that sucrose and glycerol formed hydrogen bonds with hydroxyl groups to prevent the formation of hydrogen bonds between the microfibrils [2]. There has been confusion as to why sodium chloride cannot prevent the loss of paper strength despite the fact that electrolytes were regarded as effective in interfering with hydrogen bonding [1]. Laivins and Scallan suggested that sucrose and glycerol work as bulking agents within the fiber wall [1]. If their suggestion is true, then a lower molecular weight chemical should be more effective. However, no further work focused on whether the previous claim is correct or not.

It is known that wet fiber flexibility has an effect on the ability of fibers to form bonds with each other, one of the important factors affecting paper strength. The wet fiber flexibility is considered to be related to water retention value (WRV), an index of fiber swelling. In many articles, WRV is used as

representative of the degree of fiber flexibility [3-5]. It is desirable to know individual fiber flexibility. Although there are many techniques that could be used for the measurement of individual fiber flexibility, few studies have focused on the effect of chemical treatments on fiber flexibility.

It is recognized that dry strength agents can improve paper strength. Higgins and McKenzie also observed that adding some dry strength agents to virgin fibers could benefit the strength of recycled paper [2]. Dual-polymer dry strength programs were found to be more effective for paper strength [6-8]. It is of interest to know whether the effect from the dual-polymer programs can carry over to recycled paper when the chemical treated original fibers are recycled.

To date, many studies have focused on the effect of recycling on tensile strength. One of the important performance characteristics for linerboard is to produce corrugated containers that protect contents from compression forces during packing, storage and distribution. Old corrugated containers (OCC) are the most significant category of waste papers for recycling based on the percentage of recovery rate and by tonnage [9]. However, the effect of recycling on the compression strength of recycled OCC has not yet received as much attention as it deserves, considering the importance of this issue.

The objectives of this study are summarized as follows:

1. To better understand the mechanisms of paper strength loss due to recycling in the case of unbleached kraft softwood fibers.
2. To determine the role of chemicals added to never dried pulp, with respect to the strength of virgin and recycled paper.

3. To identify and confirm the mechanisms that control the effects of chemicals on the recycled paper strength.

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CHAPTER 3

Effect of Chemical Pretreatments of Never-Dried Pulp on the Strength of Recycled Linerboard*

ABSTRACT

According to the American Forest and Paper Association (AF&PA) the recovery rate of corrugated boxes used in the US now exceeds 75%. In principle the recycling of boxes saves fiber resources, requires less total energy and is economical. However, further progress in old corrugated container (OCC) recycling faces a potential barrier. It is known that recycled kraft fibers have a reduced bonding ability. The tensile strength value was observed to fall by 25-35% when the same fibers were reslurried and then formed into a second generation of paper. The approach taken in this study was to pre-treat the never-dried fibers before the first cycle of papermaking. Tests were carried out to shed light on the mechanism of strength loss and the effects of chemicals relative to strength loss when paper is dried and then recycled. New data have been obtained with never-dried, refined, unbleached kraft pulp. Pretreatment with various chemical agents was able to compensate for some of the strength loss. Two general classes of treatment agents were identified that were able to favorably affect the strength of recycled sheets. Certain low-molecular weight materials such as sucrose appeared to interfere with the mechanism of pore closure during the initial drying. The sucrose-pretreated fibers retained higher levels of water retention value (WRV), indicating a greater degree of swelling

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when the once-dried fibers were placed back into water. These results with sucrose are consistent with a mechanism in which loss of bonding ability is related to irreversible closure of pores in the fiber cell wall. In contrast, certain high-mass polyelectrolytes such as guar gum products, cationic starch, and polyelectrolyte complexes appeared to affect the adhesiveness of the fiber exteriors of the recycled fibers. These polymeric chemicals increased the relative strength of both the primary and secondary sheets, but there was no effect on the water-holding ability of the fibers. It is proposed that the mechanistic role of these polymers is related to effects on relative bonded area or shear strength of bonds per unit of bonded area.

INTRODUCTION

A revolution in papermaking technology occurred in the mid to late 1800's with the development of chemical pulping methods, including the kraft pulping method [1]. Kraft fibers were able to produce strong paper, especially when compared to groundwood fibers. The superior strength of kraft fibers is due in part to the relatively intact state of fibers that are released by chemical dissolution of the lignin that binds them together in the wood. Unfortunately, refined chemical fibers suffer an irreversible loss of bonding ability the first time that they are dried [2-4]. Howard and Bichard observed a strength loss of about 25% when refined kraft handsheets were reslurried and then made into a second generation of handsheets under matched conditions [2]. By contrast, no loss of strength occurred when mechanical fibers were recycled according to the same experimental program.

With increases in the recycling of waste paper and paperboard, there has been increased interest in the changes of fiber properties during recycling. Previous work has shown the deterioration of paper strength properties due to the loss of fiber bonding ability during recycling for chemical pulps [5-10]. The process leading to reduced bonding has been described as irreversible hornification, which implies a stiffening or hardening of the fiber [11-13].

Ellis and Sedlachek found that the fiber-fiber bond strength of recycled fibers per unit of optically bonded area is equivalent to virgin fibers if the recycled fibers received no additional refining [11]. This implies that the weakness of the recycled paper sheet is due largely to the inability of the fibers to develop bonded area.

Berthold and Salmén [3] showed differences between kraft and mechanical pulps that help explain the different responses to drying. The process of kraft pulping and subsequent bleaching treatments were found to change the distribution of micro-pores within the fiber cell wall. Thermomechanical pulp (TMP) fibers were found to have many pores with a mean diameter of about 1 nm; larger pores did not contribute significantly to the net pore volume. By contrast, kraft and bleached kraft fibers had increased populations of pores in the size range of about 5 to 20 nm. Presumably these micro-pores of intermediate size resulted from the removal of lignin from the cell walls during pulping and bleaching.

Results reported by Gruber *et al.* [4] provide evidence as to what happens to the pores of kraft fibers during successive cycles of drying, as in the case of a

fiber that has been recycled several times. These workers evaluated the adsorbable amounts of highly charged cationic polymer samples having three different molecular masses. The greatest amount of adsorption was achieved with the lowest-mass polymer. This was explained in terms of the ability of the small polymer to penetrate into small pores. The adsorbable amount of polymer on untreated pulp was decreased with each cycle of drying and redispersal.

The cited results support a hypothesis presented by Stone and Scallan [14]. These authors proposed that drying of delignified pulp causes irreversible closure of pores. Further it was proposed that such closure of pores is part of the reason that recycled kraft fibers do not develop as high bonding strength, compared to never-dried pulps. Though refining can restore some bonding ability, it has been found that dried kraft fibers tend to fragment to a greater extent compared to the corresponding never-dried fibers [15]. Again, the explanation given to explain the brittleness of kraft fibers involved the mechanism of pore closure.

Using the water retention value (WRV) as a measure of the internal fiber swelling capacity [16], recycled pulp has a less swollen nature in comparison with the never-dried pulp [5, 7, 11-14, 17-19]. This closure of the pore structure has also been demonstrated by the fact that the fiber surfaces become less susceptible to enzymatic attack [20].

Previous attempts to overcome the strength loss of kraft pulps almost always have involved attempts to restore bonding ability to fibers that already have been dried. For instance it is well known that bonding properties can be enhanced by the addition of dry-strength agents such as cationic starch [21].

Such agents, when added to the fiber slurry, appear to increase the relative bonded area or the strength per unit area of bonds between adjacent fibers [22]. Alternatively, it has been possible to restore swelling ability to dried fibers by treatment with caustic solutions [23], specialized refining regimes [15, 24], and hydrothermal treatments [25-26]. While each of these approaches has potential to produce strength benefits, the capital costs and operating costs have discouraged their wider adoption within the industry.

The approach taken in the present work was to add chemicals to the refined, never-dried fibers before the first cycle of sheet forming [27-28]. The intent is to compare and understand the effects of various non-reactive, water-soluble materials. In principle such materials have the potential for low-capital implementation in existing paper machine systems. Results from treated pulps were compared to recycled controls that had not been chemically pretreated before the initial cycle of papermaking. WRV tests were conducted as a means of clarifying the mechanism by which various chemicals affected recycled paper strength. The objective was to find out if there is a correlation between chemicals' effects on the water-swelling ability of recycled fibers versus recycled paper's strength. Such a relationship would tend to support pore closure as a key mechanism responsible for strength loss during recycling.

Tests with chemical additives of relatively high molecular mass were carried out to determine if significant strength gains could be achieved by mechanisms unrelated to pore closure. Past work has shown that molecules having molecular mass values much higher than 20,000 g/mole tend to remain externally on the

fiber surfaces during the time scales associated with the addition of paper chemicals before paper is formed [4, 14, 29]. In principle such additives would be expected to increase either the relative bonded area or the bond strength per unit of bonded area [22, 30]. An advantage of adding polymeric materials to the virgin fibers is a possibility of improving properties of the virgin paper. However, the focus of the work reported here was to find out to what extent the dry-strengthening effects of chemicals were carried over to the recycled paper, made from the same virgin paper without further chemical addition.

Unbleached kraft pulp is a major component in the furnish of linerboard. One of end-use properties of linerboard is to produce corrugated container to protect contents inside box from compression forces during packing, storage and distribution. Thus, in this present study, the effect of chemical treatments on the compression strength was also considered.

EXPERIMENTAL

Materials

Pulp: Never-dried, unbleached pine kraft pulp was obtained from the Mansfield, Louisiana mill of International Paper Company. The sample was obtained from high-density storage after it had passed through the blowline and de-shive refiners. Upon its receipt from the mill the pulp was screened and centrifuged to 30% consistency. The fibers were fluffed and then refrigerated during storage. These procedures made it possible to carry out experiments from highly consistent master batches of fibers.

Chemicals: Reagent-grade sucrose (Fisher, Lot. 701806) was used without further purification. Guar products were obtained from Hercules, Inc. These included an unmodified neutral guar, Supercol®, having a molecular mass of approximately 2,000,000 Daltons, and a depolymerized, neutral guar 30 M1F, having a molecular mass of approximately 250,000 Daltons. The carboxymethylcellulose (Hercules CMC 7M) had a medium molecular mass and a degree of substitution of 0.7. The poly-diallyldimethylammonium chloride (poly-DADMAC) was Alcofix® 169, provided by Ciba Specialty Chemicals. The molecular mass is approximately 300,000 Daltons. All chemicals were used on a dry-mass based.

Procedures

Sub-batches of centrifuged pulp were taken from cold storage and refined with a laboratory Hollander-type beater (Valley Machinery, Inc.), following the procedure of TAPPI method T-200. The pulp was dispersed in the beater for 30 minutes (zero load) then refined for 20 minutes. The pulp then was screened, centrifuged to approximately 30% consistency, fluffed, and then refrigerated again until use.

Before making handsheets the refined pulp was dispersed in a TAPPI disintegrator for 5 minutes. As shown in Fig. 3-1, chemicals were added to slurry samples of refined pulp. Addition levels were based on the added amount of chemical solid compared to the mass fiber (dry basis). The pulp samples were mixed with chemicals for 12 hours with stirring. The procedure of TAPPI Standard Method T-205 was used, with the following modifications. Instead of

the standard slurry pulp consistency 0.3%, a 0.6% consistency was used. As a result the basis weight of handsheets was 120 g/m², not 60 g/m². At the higher basis weight the samples are not expected to fail in a "buckling" mode during STFI compression strength tests [31-32]. Instead, they are expected to fail by the desired shear/internal bond failure. Rather than drying the sheets under a constant humidity condition, the handsheets with drying rings were placed in an oven at 105 °C for eight minutes in order to simulate the effect of drying on a paper machine. After that the handsheets were stored in a TAPPI standard condition room for 12 hours before testing. The procedure of making recycled handsheets was the same as primary handsheets, except without further chemical addition.

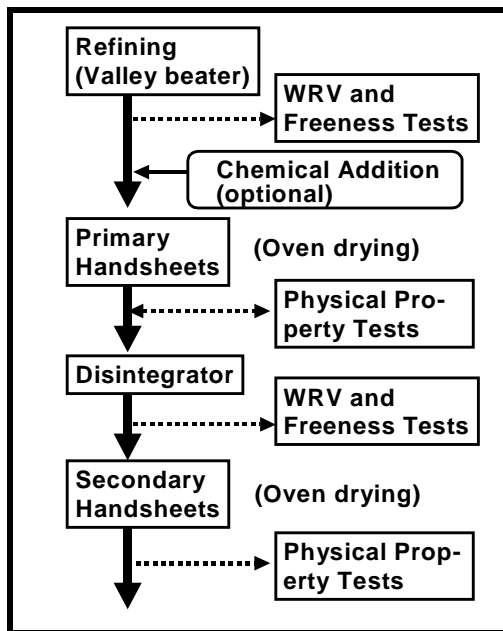


Fig. 3-1. Procedure for tests involving pretreatment of never-dried refined pulp, followed by sheet forming and recycling

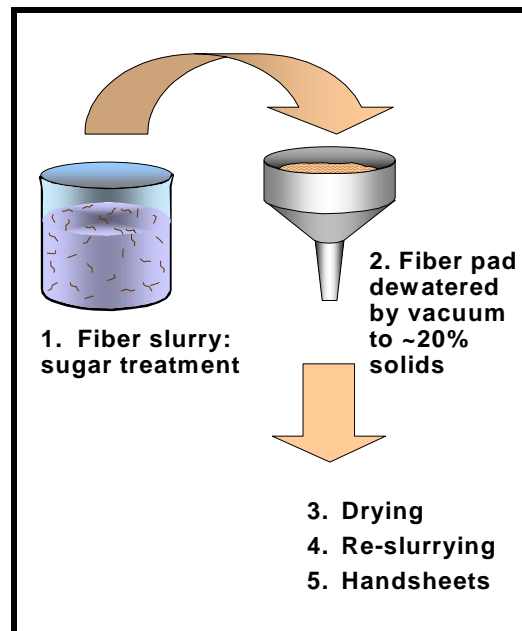


Fig. 3-2. Procedure for tests in which the virgin pump was dried in the presence of concentrated sugar solutions

Water retention value (WRV) is an important index in this experiment because WRV measures the internal fiber swelling capacity. The higher the value, the more the swelling capacity is. The procedure followed TAPPI Test UM 256 with some modifications. Prior to measurement, the pulp was dispersed in a disintegrator for 5 minutes [15,000 revolutions], thoroughly washed in a large excess of deionized water, and allowed to stand in deionized water overnight. Following further washing the pulp was collected on a vacuum filter and dewatered to 25% solids. Moist samples of pulp (equivalent to 0.16 g dry weight) were placed in sintered centrifuge tubes (pore size 0.22 μm , volume 3 ml, provided by MSI). Samples were centrifuged at 900 g for 30 minutes according to TAPPI UM 256. After centrifuging, the moisture content of the samples was determined by weighing immediately and also after drying at 105 °C for 2 hours and cooling in a desiccator jar for 30 minutes.

The procedures used to evaluate effects of sugars were different from those used with other chemicals. As shown in Fig. 3-2, instead of forming primary handsheets, a pad of fibers was formed on a Büchner apparatus with vacuum applied. The fibers were dried under TAPPI standard conditions, instead of oven drying. As noted in an extended abstract from an earlier presentation of our work [33], sugar had a positive effect on tensile strength.

RESULTS AND DISCUSSION

Table 3-1 summarizes the results for refined virgin pulp without chemical treatments. The Canadian Standard Freeness of the pulp used in the experiment

was 675 ml. Although this is high for many paper grades, it is typical for making virgin unbleached linerboard.

Compression strength of the linerboard is a key predictor for corrugated containers that will be stacked to a certain height during storage and shipping [33-34]. As shown in Table 3-1 the STFI compression strength of handsheets formed at 675 ml freeness dropped by approximately 17% when the dried handsheets were dispersed to form recycled handsheets under same forming and drying conditions. The breaking length of the handsheets decreased as well.

Table 3-1. Properties of paper made from refined virgin pulp vs. paper made from oven-dried pulp

Test Items	Units	Never-Dried	Recycled	Change %
Canadian Std. Freeness	ml	675	642	
Basis Weight	g/m ²	130.5	128.8	
Caliper (thickness)	10 ⁻³ in	7.3	7.7	
Apparent Density	g/cm ³	0.71	0.66	
Elmendorf Tear Strength	g _r	388.0 ± 35.8	488.4 ± 94.7	12.6
Tensile Strength	KN/m	7.512 ± 0.470	5.599 ± 0.250	
Breaking Length	Km	5.868 ± 0.367	4.431 ± 0.198	-24.5
STFI Compression	Klb _r -ft/lb	8.749 ± 0.603	7.297 ± 0.543	-16.6
Water Retention Value	%	212.6 ± 5.6	166.7 ± 3.3	-21.6

Effects of Treatment with Sucrose

One hypothesis for the mechanism of strength loss is that pore closure increases the degree of crystallization at the fiber surface and so decreases fiber-fiber bonded area. If this mechanism is true, then it ought to be possible to inhibit pore closure during drying by the addition of chemicals that are small enough to fit into pores. Sucrose was chosen for this experiment because the molecular diameter of sucrose is approximately 1.5 nm [34], which is less than the characteristic pore sizes of kraft fibers [14]. Fibers were soaked in a solution of 2% sucrose by mass for 12 hours, formed into pads on a Büchner funnel, and

dried. Then they were formed into “recycled” handsheets. As shown in Fig. 3-3, it was found that adding sucrose to virgin refined pulp increased the tensile strength of recycled handsheets, relative to the recycled control. This observation is consistent with a hypothesis that sucrose inhibited the closure of pores and helped to preserve the bonding ability of the fiber surfaces.

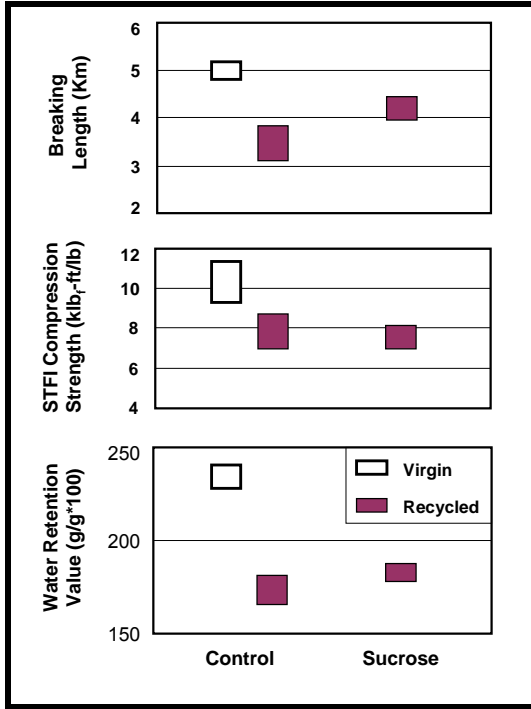


Fig. 3-3. 95% confidence intervals for samples pretreated with concentrated sugar solutions (fiber-pad method)

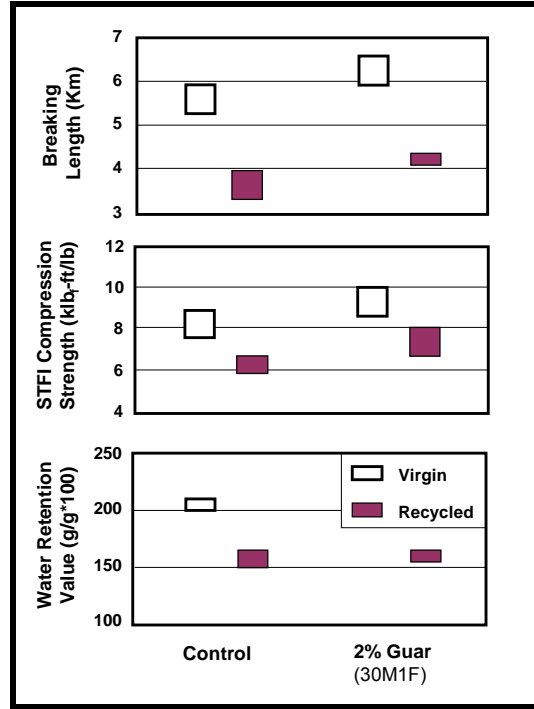


Fig. 3-4. 95% confidence intervals for a control and for samples pretreated with 2% depolymerized guar gum

Results of water retention value tests gave at least partial support to the hypothesis that sugar is able to block a strength-loss mechanism involving pore closure. The water retention value of reslurried fibers that had been air-dried in the presence of concentrated sugar was 182%, compared to 171% in the case of the control. Presumably this means that the sugar treatment either prevented closure of the pores in the cell walls or made it possible for them to reopen more easily when the dried fibers were rewetted. It was noted, however, that oven

drying of fiber pads reduced the WRV numbers; fibers oven-dried in the presence of sugar had a WRV value of 167%, compared to 158% in the case of the untreated pulp.

A puzzling aspect of the results shown in Fig. 3-3 was the fact that there was no corresponding benefit in terms of the compression strength of the recycled paper, when the fibers were dried in the presence of sucrose. This observation of a tensile strength increase without a compression strength increase suggests that something may have changed relative to the paper structure or the predominant failure mechanism. Work is under way to determine whether the divergence in strength property effects might be due to residual sugar in samples prepared in the described manner. Preliminary results suggest that 0.34% sucrose (dry basis on dry fiber mass) was present in the recycled sheets made from paper that had been dried in the presence of 2% sucrose solution. It is possible that the residual sugar made the structure more pliable and more prone to compressive failure at a given level of tensile strength.

The fact that the tensile strength benefit due to sugar occurred both during the first generation of sheet formation and also in the recycled pulp will prompt further theoretical and practical study. In the classic work by Higgins and McKenzie [28] it was assumed that the main effect of sugar was to inhibit mechanisms leading to strength loss during drying. In light of the new results, those assumptions will need to be reviewed. The present results suggest an alternative mechanism. That is, the sugar may have acted directly or indirectly to

increase effective strength of the paper due to its presence. Further work is planned to clarify this point.

Effects of Treatment with Guar

As shown in Fig. 3-4, adding 2% depolymerized neutral guar gum 30M1F solution (based on the OD. Pulp) to virgin refined pulp furnish improved paper strength not only for primary handsheets but also for secondary handsheets. In this case the water retention value did not improve compared with the control experiment. This observation is consistent with reasonable estimates of the molecular size of dissolved guar molecules. Assuming a molecular mass in the range 100,000 to 2,000,000 Daltons, work with dextrans would predict values in the range 14 to 56 nm for the effective diameters of the dissolved molecules [34]. Therefore it is unlikely that guar would be able to enter 5-20 nm pores in sufficient quantity to prevent their closure or affect their ability to reopen when the pulp is redispersed.

One hypothesis to explain increasing paper strength in this case is that guar prefers to stay on the fiber surface. The affinity between natural guar and cellulose has been attributed to a similar molecular structure and hydrogen bonding ability [35-38]. These attributes also are consistent with increased relative bonded area or strength per unit area [22].

Results of further tests are consistent with the explanation that most of the guar still remains on the fiber surface even after dried paper is redispersed. Thus, when the recycled handsheets were formed without additional guar, the benefits of the original treatments were passed on to the recycled handsheets.

Tests comparing two un-derivatized guar products of differing molecular mass helped to confirm this hypothesis. The natural, non-depolymerized neutral guar (Supercol®) has higher mass than 30M1F. As shown in Fig. 3-5, adding 1% of the natural guar increased the strength of recycled handsheets, especially the tensile strength. By comparison with Fig. 3-4, this increase was greater than in the case of the lower-mass guar, 30M1F. The proposed reason is that the higher molecular mass product is more capable of filling the void areas between fiber surfaces, increasing the relative bonded area and increasing bond strength.

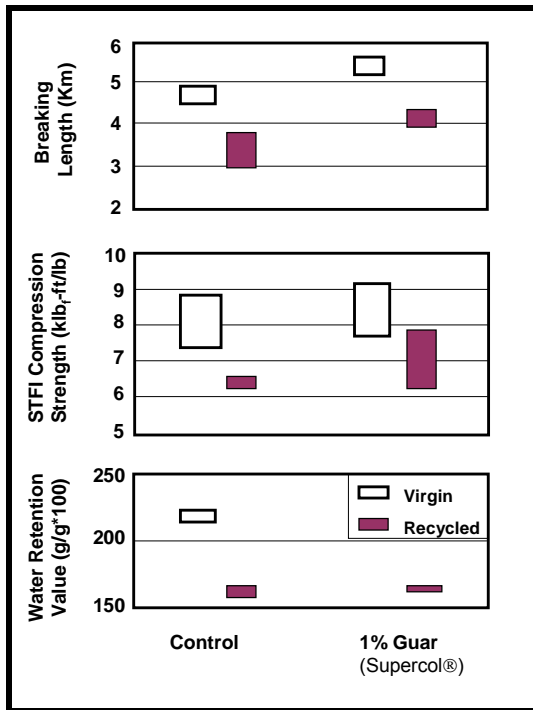


Fig. 3-5. 95% confidence intervals for a control and for a sample pretreated with high-mass, underivatized guar gum

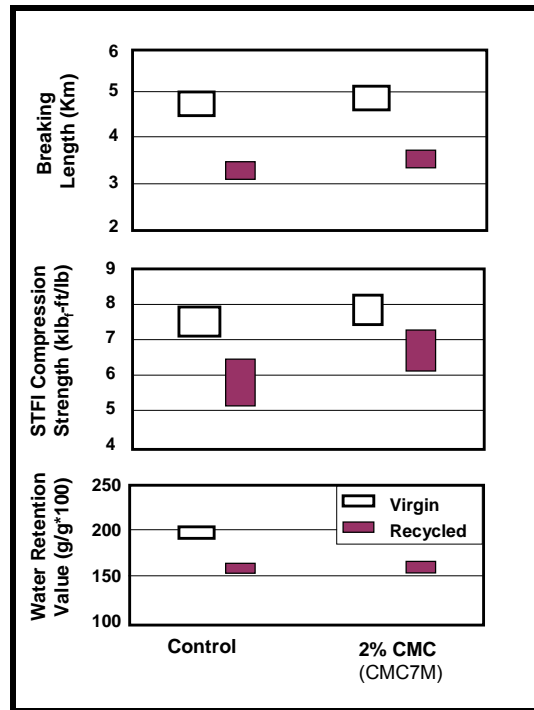


Fig. 3-6. 95% confidence intervals for a control and for a sample pretreated with carboxymethylcellulose (CMC)

Effects of Treatment with Carboxymethyl Cellulose

As shown in Fig. 3-6, a 2% addition level of carboxymethyl cellulose (CMC 7M) benefited recycled paper strength relative to an untreated control. At an

80% level of confidence pretreatment of the fibers with the CMC increased the compression strength of the recycled sheets relative to the sheets made from recycled fibers that had not been pretreated. This effect is consistent with the reported effect of carboxyl groups at the surfaces of fibers promoting strength of recycled papers [12], except that in the present case these carboxyl groups belong to polyelectrolytes that may adsorb onto the fiber surfaces.

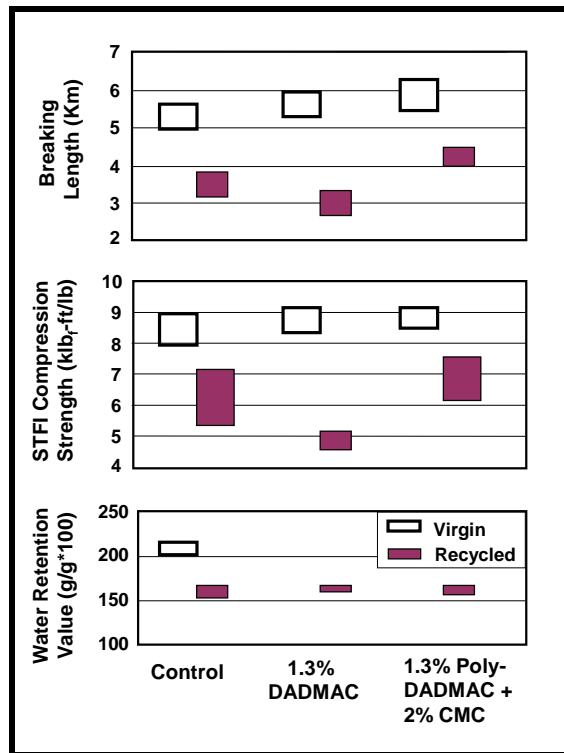


Fig. 3-7. 95% confidence intervals for a control, for a sample pretreated with just polyDADMAC, and for a sample pretreated with polyDADMAC, followed by CMC

Figure 3-7 shows another strategy to increase the paper strength. The low molecular mass poly-DADMAC did not have a significant effect on fines retention. Evidence regarding fines retention came from the fact that the addition of 1.3% poly-DADMAC (based on OD pulp) caused no significant change in paper mass. However, the chemical had a significant negative effect on the

strength of the recycled handsheets. By contrast, addition of 2% CMC7M after adding 1.3% low molecular mass poly-DADMAC to the virgin pulp slurry, the recycled paper strength was increased markedly compared with control experiment. This was especially true for breaking length.

To explain the beneficial combination of poly-DADMAC and CMC it was inferred that the cationic DADMAC stayed on the fiber surface by electrical attraction. The negatively charged CMC then could use the charged patches of poly-DADMAC to anchor itself to the fiber surfaces. Fibers were connected not only through direct hydrogen bonding, but also through the anionic CMC. The CMC is able to form hydrogen bonds effectively with cellulose, due to their chemical similarity. As a consequence it is reasonable to assume high bond strength per unit of bonded area. Before forming another generation of handsheets, the handsheets were soaked for 4 hours and dispersed with a disintegrator. The fibers were easy to disperse, suggesting that the fiber-fiber bonds formed by the CMC were very reversible. It is assumed that the poly-DADMAC helped to hold the CMC on the fiber surface during repulping, allowing its benefits of the dry strength agent to pass on to the recycled handsheets.

This proposed mechanism for poly-DADMAC and CMC differs from what is expected for very high molecular mass cationic polymers, *i.e.* retention aids. Retention aids are expected to function as bridges between adjacent fibers. Such bridges are strong enough, in many cases, to cause persistent flocculation of fibers, which hurts the uniformity of the paper. By contrast, the poly-DADMAC is not expected form strong bond strength with fibers or CMC because of its

lower molecular mass. It can be assumed that at a certain ratio of DADMAC and CMC will optimize the effect. The different levels and charges of DADMAC and CMC may produce different results. Further work is planned to clarify this point.

The findings reported in this article have prompted additional questions related to the effects of other additives, the relative proportions of additives, and the effects of process conditions such as refining. Follow-up research will be addressed in future publications.

CONCLUSIONS

This report shows that pretreatment of refined, never-dried kraft fibers provides benefits for paper strength over primary and recycled handsheets. Evidence is consistent with three hypotheses of how chemical pretreatment can benefit the strength of recycled paper, depending on the type of chemicals used in pretreatment.

1. Drying of refined, never-dried kraft fibers in the presence of sucrose appeared to benefit the strength of recycled sheets by protecting the fibers from pore closure during drying or by making it easier for such pores to reopen when the paper was redispersed in water.

2. Neutral guar appeared to benefit recycled paper strength by increasing the affinity between fibers. This effect may be attributed to a similar molecular structure and hydrogen bonding ability between the polymer and the fiber surfaces. Results are consistent with guar remaining on the fiber surfaces during recycling.

3. Treatment of the fibers with low molecular mass poly-DADMAC, followed by CMC appeared to benefit the strength of recycled paper to a degree that could not be explained by the effects of the individual additives alone. The proposed mechanism is that the bonding between the low molecular mass DADMAC, the CMC, and the fiber surfaces is reversible. The bonds are not difficult to break during dispersing so that the chemicals are free to act as strength aids during manufacture of recycled handsheets. Again, these results are consistent with the chemicals remaining on the fiber surfaces during recycling.

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CHAPTER 4

Can Recycled Kraft Fibers Benefit From Chemical Addition Before They Are First Dried*

ABSTRACT

The goal of this work is to overcome the loss of bonding strength experienced by kraft fibers when they are dried and reslurried. Paper strength was compared in the presence or absence of chemical pre-treatments of the refined, never-dried pulp. Polyelectrolytes of relatively high molecular mass had the greatest beneficial effect on the compression strength of recycled unbleached kraft paper. Results were consistent with the persistent nature of charged complexes formed by polyelectrolytes at fiber surfaces, and the contribution of such complexes to inter-fiber bonding, even after drying and recycling. Differing effects of certain chemicals on compression versus tensile tests suggest that chemicals can affect not only the extent, but also the physical properties of inter-fiber bond sites.

INTRODUCTION

In 1963 Higgins and McKenzie had a radical idea: treat kraft pulp fibers before they are ever dried in order to improve the strength properties when the once-dried fibers are made into paper [1]. The idea was radical because of the times. Relatively little paper was being recycled, and people were more concerned about strength losses during production of dry-lap pulp. Subsequent work has shown that strength loss is more important in the case of refined pulp

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for papermaking, compared to the production of dry-lap pulp, which is unrefined [2]. To put things in perspective, the utilization rate of waste fibers (OCC) in recycled containerboard in 1963 was reported as 21.1% in the U.S. [3]. In 2001 OCC comprises about 67% of the fiber for U.S. containerboard production [4], and the recovery rate of old corrugated containers is approximately 70% when exports are considered [5-6].

All of the treatments discussed in this article will be of the same nature as those described by Higgins and McKenzie [1] – chemical additions to never-dried pulp used to make first-generation handsheets, and then nothing added when making the recycled (2nd generation) handsheets. The cited work identified several types of chemical treatments that yielded measurable improvements in the bonding strength of recycled handsheets, compared to untreated kraft handsheets that had been repulped and formed again. In subsequent years there have been many studies that have added greatly to our understanding of how the drying of kraft fibers can cause essentially irreversible losses in bonding ability [7-22]. A few innovative studies have shown that chemical derivatization of fiber surfaces sometimes can prevent strength losses from occurring [20-22]. However, relatively little published work describes pre-treatment with non-reactive chemicals that can be added to fibers under typical papermaking process conditions [22-24].

Higgins and McKenzie obtained encouraging results with simple sugars, but very high concentrations were required [1]. Those tests have been replicated by others, including the present authors [22, 24]. Sugars at very high

concentrations appear to inhibit some changes in the fiber surfaces and pores caused by drying [1, 7, 22], even though they have little affinity for the fiber surface [25]. These results show the mechanism of strength loss; however papermakers have not rushed to add sugars to their process.

The present study focuses on chemical pre-treatments that are more likely to adsorb from solution onto fiber surfaces. Unbleached kraft pulp of relatively high freeness was selected for this work because of its importance for the most highly recycled grade of paper, old corrugated containers (OCC) [26].

Given the relative scarcity of data related to the effects of additives on the bonding potential of fibers after they are recycled [22-24], the experimental approach chosen for this initial phase of the project may be described as a “screening” study (see Experimental). Factors used for selecting a range of contrasting candidate materials for the screening tests included the following: (a) presence and degree of carboxylic acid content or other anionic groups, (b) presence and degree of cationic groups, (c) presence of hydrophobic groups, and (d) molecular mass and structure. Self-imposed constraints on the strength-enhancing strategies considered in the work reported here included the following:

- Additives should be water-soluble and non-toxic.
- Additives reported here are added only to the refined, never-dried pulp, not later.
- Other than chemical preparation and feeding, no additional unit operations, *e.g.* washing stages, should be required.

- The main focus is the strength of the “recycled” paper, following a cycle of virgin handsheet forming, oven drying, reslurrying, and secondary sheet formation without further refining or chemical addition.
- A condition is to be considered “successful” if the treatment not only improves the strength of the recycled paper, but also gives either a positive effect or no significant effect on the strength of virgin sheets.

THEORY

There are at least two ways in which a non-reactive chemical added to never-dried fibers could affect the strength of recycled paper. As illustrated in Fig. 4-1, one can expect different results if the additive is absorbed into the fiber cell walls (Case A) versus those that tend to stay at the outer surfaces (Case B). Past work has shown that pores in the cell walls of kraft fibers are readily penetrated by water-soluble monomers, as well as by oligomers up to about 10,000 Daltons [25]. In principle, much larger macromolecules may absorb into the 5-20 nm slit-like pores of a typical never-dried kraft pulp fiber by a process of reticulation, *i.e.* snake-like movement [27]. In practice, there is insufficient time during papermaking operations for the system to approach an equilibrium state [28]. It is safe to assume that macromolecules in excess of 100,000 Daltons do not substantially penetrate into the fiber [25] during typical time periods of contact between the additives and paper fiber slurries. There are excellent reviews describing factors governing adsorption of macromolecules onto surfaces [28-30].

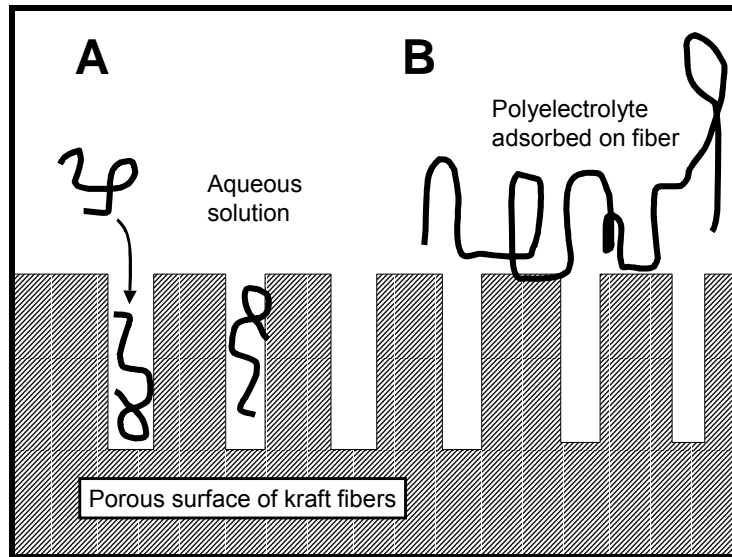


Fig. 4-1. Modes of chemical interactions with fiber surfaces

Case A: How a molecule in a fiber wall may affect recycling

Let's first consider the possible mechanistic role of a chemical additive that has penetrated into a never-dried fiber. There are at least four ways in which past work suggests a likely bond-enhancing role for chemicals absorbed into the walls of never-dried fibers:

1. As in the pioneering work of Higgins and McKenzie, simple, non-interacting molecules such as a sugar might inhibit closure of pores when the fiber is dried [1]. Presumably the hard-to-reverse closure of submicroscopic pores results in less conformable fiber surfaces [31], yielding a reduction in relative bonded area [32]. The effects of sugar on the strength of recycled kraft fibers have been confirmed in subsequent work by us and by others [22, 24]. To the extent that this mechanism is active, one would expect a corresponding effect on results of water retention value (WRV) tests of the once-dried fibers [33-36].

2. It is also reasonable to expect that substances filling the pores spaces of fibers can act as either plasticizers or stiffeners of the cell wall material [37-38]. In cases where this mechanism is important, one ought to be able to observe characteristic effects on strength properties of the recycled paper. For example, compression strength is expected to be critically dependent on individual fiber stiffness [39-40]. Fiber stiffness is expected to increase as a consequence of pore closure and other processes during drying [41]. By contrast, tensile strength does not require stiff fibers, and a more compliant fiber surface can be expected to result in greater relative bonded area of the recycled paper [32].

3. Results reported by Ehrnrooth *et al.* [20] suggest that hydrophobic groups might affect strength of recycled fibers. A moderate degree of acetylation of fiber surfaces increases the bonding ability of fibers and the increased bonding ability remains in effect when the fibers are reslurried and formed into recycled sheets. One explanation is that the acetyl groups inhibited formation of hard-to-reverse intra-fiber hydrogen bonding [10, 22]. Evidence is not clear as to whether or not the inability of pores to reopen when the fibers are rewetted is due to local crystallization of newly joined cellulose surfaces [42], or other factors [15, 17, 43-44]. In any case, this mechanism suggests that various substances containing hydrophobic groups ought to be included in the screening study.

4. Finally, Lindström and Carlsson [10] showed that it is possible to avoid strength loss during the drying of kraft fibers when two conditions are met. First, the fiber surfaces must have a sufficient density of carboxylic acid groups, an effect that can be achieved in the laboratory by carboxymethylation. Second, the

fibers must be dried in a pH range favoring dissociation of those acid sites, *i.e.* when there are negatively charged surfaces. One ought to expect the same effect if non-reacted carboxylated species can be persuaded to remain in the pores of kraft fibers. Some “persuasion” strategies considered in the present work included the use of cationic materials or groups [29-30], or hydrophobic groups [1, 45-46]. Other screening tests were carried out with materials of different molecular mass to achieve a balance between high-affinity adsorption [30] and ability to penetrate into small pores [25].

Past work suggests that monomeric dye molecules can benefit paper strength, especially if they are present during refining [47]. While it should be noted that present experiments followed a different procedure, it is worth noting that dye molecules combine the features mentioned in items 3 and 4 above. The hydrophobic character of the chromophoric groups within a dye is expected to help in its adsorption [48]. Variation of the number of anionic groups, per molecule of dye or fluorescent whitening agent offers a possible way to achieve the best balance between adsorption tendency and a possible impact on strength loss during drying.

Case B: How additives on a fiber surface may affect recycling

Literature related to dry-strength additives leaves little doubt that water-loving polyelectrolytes adsorbed at fiber surfaces can act as bonding agents [49-53]. Effects of starch and guar derivatives, and acrylamide copolymers are usually attributed to increased relative bonded area [32, 54]. In certain cases the

data are consistent with increased shear strength of inter-fiber bonds, per unit of area that appears to be bonded, based on light scattering analysis [55].

Less is known about the degree to which the same additives also can contribute to strength when the same fibers are recycled. The ability of an additive to contribute to bonding the second time around when fibers are recycled ought to depend on (a) whether the additive remains adsorbed, and (b) whether the additive is degraded, matted down onto the fiber surfaces, permanently dehydrated, or lost into the cell wall in the course of drying, use, and redispersal of the waste fibers. The approach taken in the present work was to compare a range of contrasting materials. Variations in molecular mass, charge type and density, and the inclusion of materials with hydrophobic groups in the pool of candidate treatments can be expected to affect both adsorption [28-29], and possible mechanisms by which the cell wall loses its bonding ability [7, 15, 17-21].

Carboxylated polymers at a fiber surface might be expected to benefit the bonding ability of the fibers when they are recycled, but only if they remain adsorbed there. Anionic polyelectrolytes typically do not adsorb well on anionic surfaces of kraft fibers. Possible exceptions include guar gum products; these are reported as having special affinity for cellulose [56]. Another exception is hemicellulose; hemicellulose that originates with the wood appears able to stay on kraft fiber surfaces and contribute to bonding in recycled sheets [57-58]. A common feature of typical guar and hemicellulose products is that they are relatively low in anionic charge. An approach used in this work was sequential

addition, following a cationic polymer. Figures 4-2 and 4-3 illustrate ways to envision what may happen at a molecular level. In these figures black curves correspond to cationic polyelectrolytes and gray curves correspond to anionic polyelectrolytes.

Figure 4-2 corresponds to a proposed “mordant and glue” model. Here the cationic polymer is added first, taking advantage of its expected high-affinity adsorption to the fiber surfaces [29-30]. The cationic polymer then can serve as a point of attachment for an anionic dry-strength agent such as carboxymethylcellulose (CMC). Addition sequences roughly corresponding to the “mordant and glue” model have been reported in work focusing on the strength of the first generation of paper [59], but no corresponding results have been reported for residual effects of such treatments after fibers are recycled.

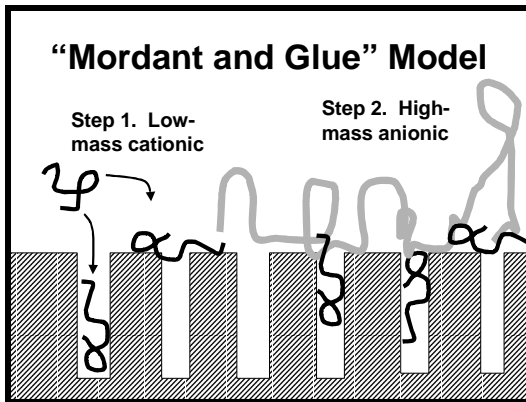


Fig. 4-2. Proposed mechanism for dual treatment of fiber surfaces

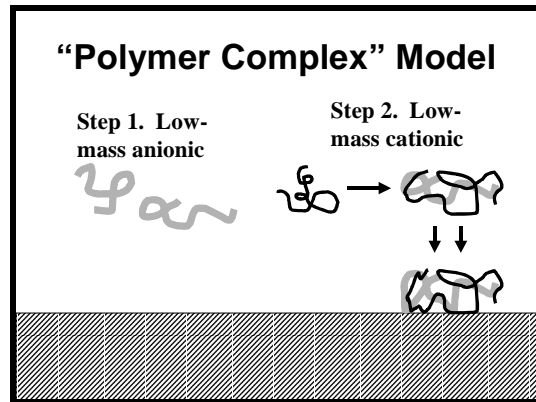


Fig. 4-3. Alternative mechanism involving complexation of polyelectrolytes

Figure 4-3 shows a limiting model that helps to justify experiments with the opposite order of addition. This “polyelectrolyte complexation” model requires that the two additives have sufficient mobility and time to form a complex [60]. This model might reasonably be applied in the case where the first additive is an

anionic polymer having a low affinity for the fiber surfaces. Subsequent addition of a cationic polyelectrolyte is then expected to result in precipitation of insoluble complex onto the fiber surfaces. If this type of model is valid, then it is reasonable to expect results to be dependent on contact times, agitation, and orders of addition. Others have considered polyelectrolyte complexes in relation to paper strength [61-64], but no publication has considered possible effects of such treatment persisting after those fibers are recycled.

EXPERIMENTAL

Materials

Never-dried, unbleached pine kraft pulp was obtained from the Mansfield, Louisiana mill of International Paper Company. The sample was collected from high-density storage after the blowline and de-shive refiners. Fresh pulp was screened and centrifuged to 30% consistency. The fibers were fluffed and then refrigerated during storage. These procedures made it possible to carry out experiments from highly consistent master batches of fiber.

Starch products from Penford Products Co. included PenCat® 550, a cationic quaternary ammonium derivative having 0.27% nitrogen by mass. "Anionic starch" consisted of Astro® Gum 3010, having approximately 1% carboxymethylation. "Oxidized starch" was Douglas® 3018, with approximately 0.3% carboxylation. "Hydroxymethyl starch" was Penford® Gum 280.

The "anionic acrylamide copolymer" was Hercobond® 2000, a copolymer based on 92 mole % acrylamide groups and 8 mole percent acrylic acid, yielding a charge density of 1.1 microequivalents per gram.

Guar products provided by Hercules, Inc., included the following: “Neutral guar” was Supercol® U, a product having a mass-average molecular mass of about 2 million Daltons. “Depolymerized neutral guar” (code 30M1F) was unsubstituted and had a molecular mass of 200,000 to 300,000 Daltons. “Cationic guar” (SP813D) had a degree of substitution of 0.13 (800 microequivalents per gram) and a molecular mass of 1.1 million Daltons. The “depolymerized cationic guar” (SPX247) had a similar composition as SP813D, but a lower molecular mass of 500,000 Daltons. The “anionic guar” (GPX241) had a molecular mass between 1 and 2 million Daltons and a degree of substitution of 0.08 to 0.1, corresponding to 0.49 to 0.62 meq/g.

Carboxymethylcellulose (CMC) products provided by Hercules, Inc., were designated by the following codes: 7L, 7M, 7H, 9M8, and 12M8. In these codes the initial number corresponds to ten times the degree of substitution. Because each pyranose unit of cellulose has three available hydroxyl groups, the maximum theoretical degree of substitution is 3, and the samples span the most common range for CMC products. The letters L, M, and H correspond to low, medium, and high molecular mass. Typical molecular mass values corresponding to these categories are 90,000, 250,000, and 700,000 Daltons. An additional CMC product (LT446A) having lower DS of 0.35 and a molecular mass of 200,000 Daltons was obtained from Akzo Nobel. The hemicellulose was a developmental product, code 9673:83 from National Starch, and described as “corn fibre gum”. The stated purity level was 98%.

“High-mass chitosan” was a Vanson product, Natural Biopolymer SC442, a material with 83.5% deacetylation. “Low-mass chitosan” was an 85% deacetylated product, Lot 00-AESQ-0741 from the same source. The chitosan products were solubilized before use by mixing for two hours in 5% acetic acid.

The fluorescent whitening agents were Blankophor® AWP, PL, and UW from Bayer. These were, respectively, di-, tetra-, and hexa-sulfated stilbene compounds. The direct dye was Pontamine® Kraft Orange OCC, from Bayer. Sodium laurylsulfate was of reagent grade.

Low-mass poly-DADMAC was Alcofix® 169, provided by Ciba Specialty Chemicals. The molecular mass is approximately 300,000 Daltons. High-mass poly-DADMAC was Alcofix® 109, having a molecular mass of approximately 1,000,000 Daltons. All chemicals were used on a dry-mass basis.

Procedures

Sub-batches of centrifuged pulp were taken from cold storage and refined with a laboratory Hollander-type beater (Valley Machinery, Inc.), following TAPPI Method T-200. The pulp was dispersed in the beater for 30 minutes (zero load) then refined for 20 minutes. The pulp was screened, centrifuged to approximately 30% consistency, fluffed, and then refrigerated again until use.

Before making handsheets the refined pulp was dispersed in a disintegrator for 5 minutes. As shown in Fig. 4-4, chemicals were added to slurry samples of refined pulp. Addition levels were based on the added amount of chemical solid compared to the mass fiber (dry basis). The pulp samples were mixed with chemicals for 12 hours with stirring.

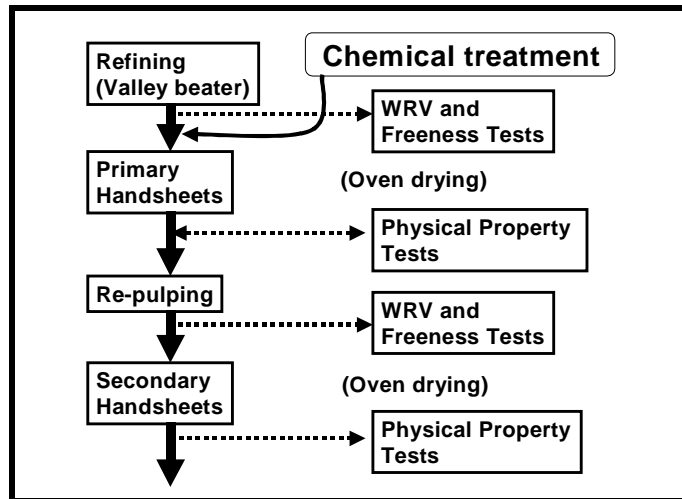


Fig. 4-4. Treatment procedure

The procedure of TAPPI Method T-205 was used, with the following modifications. Instead of the standard slurry pulp consistency 0.3%, a 0.6% consistency was used. As a result the basis weight of handsheets was 120 g/m², not 60 g/m². At the higher basis weight the samples are not expected to fail in a "buckling" mode during STFI compression strength tests [39]. Instead, they are expected to fail by the desired shear/internal bond failure. Handsheets with drying rings were placed in an oven at 105 °C for eight minutes, resulting in approximately 5% moisture content to simulate the effect of drying on a paper machine. Handsheets were stored in a TAPPI standard condition room for 12 hours before testing. Recycled handsheets were formed the same way as primary handsheets, except without further chemical addition.

Water retention values (WRV) were used to quantify fiber swelling capacity [33-36]. The procedure followed TAPPI Useful Method UM-256 with some modifications. Prior to measurement, the pulp was dispersed in a disintegrator for 5 minutes (15,000 revolutions), thoroughly washed in a large excess of de-

ionized water, and allowed to stand in water overnight. Following further washing the pulp was collected on a vacuum filter and dewatered to 25% solids. Moist samples of pulp (equivalent to 0.16 g dry weight) were placed in sintered centrifuge tubes (pore size 0.22 μm , volume 3 ml, provided by MSI). Samples were centrifuged at 900 g for 30 minutes according to TAPPI UM-256. After centrifuging, the moisture content of the samples was determined by weighing immediately and also after drying at 105 °C for 2 hours and cooling in a desiccator jar for 30 minutes.

RESULTS AND DISCUSSION

Table 4-1 shows results of tests without added chemicals. The “ \pm ” values indicate 95% confidence intervals. As shown, processes related to the preparation of secondary handsheets, including the fibers’ history of forming, drying, and reslurrying, had significant effects on water retention and physical properties.

Table 4-1. 95% confidence limits for water retention values of pulp and strength properties of resulting handsheets from untreated virgin vs. once-dried fiber

Property	Units	Virgin	Recycled
Water Retention Value	%	212 \pm 6	167 \pm 3
STFI Compression	Nm/g	26.2 \pm 1.8	21.8 \pm 1.6
Breaking Length	km	5.9 \pm 0.4	4.4 \pm 0.2
Apparent Density	g/cm ³	0.71	0.66

The first row in Table 4-1 shows a significant decrease in water retention value due to recycling. As noted by others [13], these results are consistent with a loss of pore volume when kraft fibers are dried. The observed losses in

compression strength, tensile strength, and apparent density are consistent with previous work [1-2, 8-14]. The loss of compression strength is particularly important, due to the likely failure modes of corrugated containers [39-40].

Effects of Starch Products

Pre-treatment of never-dried pulp with various water-soluble chemicals yielded changes in strength of both virgin and recycled sheets. Figure 4-5 shows 95% confidence limits for the means for typical experiments with starch products. The first pair of bars corresponds to experiments in which there was no chemical treatment. The remaining sets of bars correspond to cases in which 2% of a chemical, based on the dry mass of fiber, was added only to the refined, never-dried pulp slurry. In each case the shaded (hatched) histogram bars correspond to the STFI compression strength of sheets made from the never-dried fiber with no additional chemical use or further refining. The unfilled bars correspond to sheets made from the same fibers, after being oven-dried under the relatively mild conditions of 105 °C for 8 minutes.

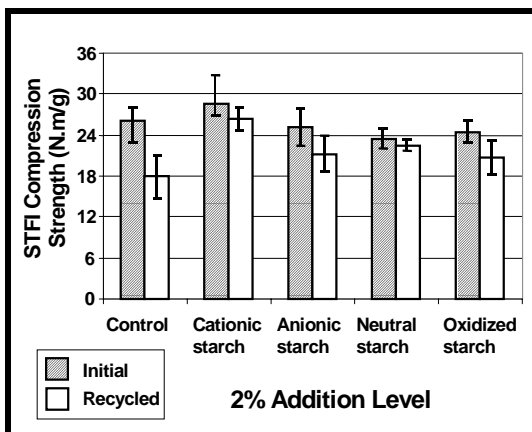


Fig. 4-5. Effects of starch products on compression strength

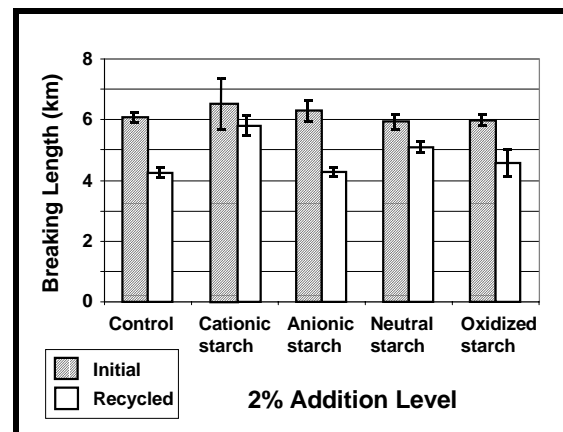


Fig. 4-6. Effects of starch products on tensile strength

A Student's t-test of the data in Fig. 4-5 indicated a significant increase in compression strength of virgin paperboard sheets at an 80% level of confidence following the addition of 2% cationic corn starch relative to the untreated virgin paper. The other starch treatments did not significantly affect STFI compression of the virgin sheets, relative to the untreated control. To place these results in context, the 2% treatment level is about twice what would be considered a typical high level for wet-end addition of starch. However, a lower retention of chemical is usual in handsheet tests compared to paper machines, since paper machines continually reuse white water for stock dilution.

Results of tests with recycled sheets in Fig. 4-5 indicated significant increases in compression strength due to all of the starch treatments, relative to the untreated, recycled control. All of these differences were significant at a higher confidence level of 90%. The recycled sheets with cationic starch treatment were stronger than the corresponding recycled control sheets by a factor of 1.47.

Figure 4-6 shows corresponding results for tensile strength. Tensile strength is not a primary indicator of likely failure modes of corrugated boxes [39-40], but the results give an indication of inter-fiber bonding [32]. The apparent increase in tensile strength of virgin pulp due to cationic starch pre-treatment was not statistically significant. But, once again, some of the starch treatments yielded increases in the strength of recycled sheets, relative to the recycled control. The largest effects were with the cationic starch, followed by uncharged, native starch, and little or no effect in the cases of anionic starches. Possibly

cationic polymers are better retained on the pulp or help to retain fines in the handsheets.

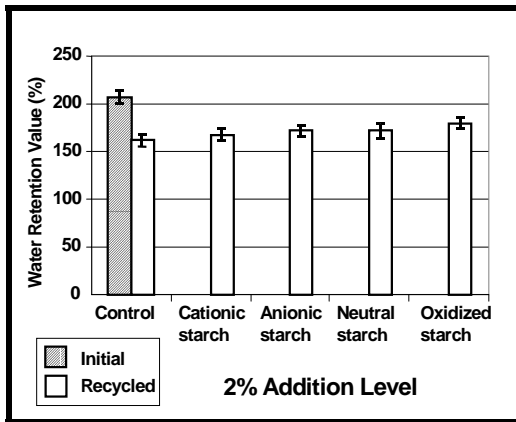


Fig. 4-7. Effects of starch on WRV

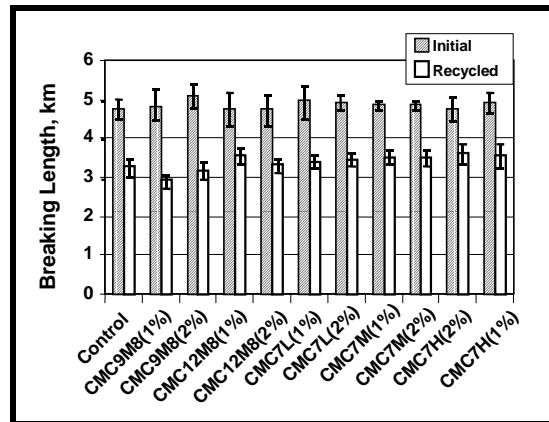


Fig. 4-8. Effects of CMC products

As shown in Fig. 4-7, pre-treatment with starch products generally increased the water retention values (WRV) of recycled fibers, relative to the recycled control. In each case the fibers were re-tested after the initial sheets were dried and then reslurried. The relative increases were significant at the 99% level of confidence, except for the case of treatment with cationic starch. The fact that the WRV numbers for the recycled, cationic-starch-treated fibers were lower than those of the other starches suggests that WRV may not be the controlling factor governing strength in this case. If one were to assume that WRV is a main indicator of strength potential, then based on the literature [33-36] one would have expected a different trend among the histogram bars in Fig. 4-7.

Effects of Carboxymethylcellulose (CMC)

Figure 4-8 compares effects of ten carboxymethylcellulose (CMC) products of different molecular mass and charge density. The labels give information about the mass and charge density, as described in the Experimental section.

As shown, there were no significant effects observed when testing virgin handsheets. Results of testing recycled sheets indicated increased strength of some treatments, compared to the untreated, recycled control.

Though the results for CMC samples by themselves were unpromising, the data will be useful as a point of reference when we later consider effects of combinations of chemicals that include CMC products. This is consistent with industry practice; CMC products are typically added in sequence with cationic polymers to achieve improvements in dry strength or to enhance the effectiveness of cationic wet-strength resins.

Tabulation of Results at the 2% Level of Treatments

The majority of the screening experiments were carried out at the 2% level of chemical treatment (dry basis) on never dried pulp mass (dry basis). Data in Table 4-2 are expressed as changes relative to untreated, control samples. For example, in the second row of data the entry “1.10” means that the cationic-starch-treated virgin handsheet had a compression strength that was 1.10 times as large as the untreated control. The second column of data shows how STFI test values of recycled sheets compared to the controls for the virgin sheets. The third column shows how the recycled treated sheets compared to the corresponding recycled control sheets; rows in the table are sorted by this column of data, with the strongest recycled sheets (relative to the recycled control) at the top of the list. Breaking length data are organized similarly. The final column in Table 4-2 shows how the water retention values of recycled sheets compared to the recycled control. The first row of data, corresponding to

“controls,” is based on pooled data from ten sets of replicated experiments, whereas the remaining rows of data are each related to control data for a given batch of fresh pulp. For this reason, the values in the first row should not be used to calculate exact relationships among the data in the remaining rows.

Table 4-2. Relative changes in strength and water retention due to drying, as affected by chemical treatment of the never-dried fiber (2% treatment level)

Chemical Additive	Change Relative To The Control							
	Property:	STFI Compression			Breaking Length			WRV
	Sample:	Virgin	Recy.	Recy.	Virgin	Recy.	Recy.	Recy.
	Control Type:	Virgin	Virgin	Recy.	Virgin	Virgin	Recy.	Recy.
UNTREATED	1.00	0.78	1.00	1.00	0.69	1.00	1.00	
Cationic starch (PC550)	1.10	1.01	1.47	1.07	0.95	1.36	1.04	
Hydroxyethyl starch (PG280)	0.90	0.87	1.26	0.98	0.84	1.20	1.06	
Anionic starch (CMAG3020)	0.96	0.82	1.19	1.03	0.70	1.00	1.06	
Cationic depol. guar (GPX247)	0.98	0.97	1.17	1.13	0.96	1.27	0.98	
Oxidized starch (D3060)	0.94	0.80	1.16	0.99	0.75	1.07	1.11	
Depolymerized guar (30M1F)	1.14	0.90	1.14	1.11	0.76	1.17	1.01	
Low-mass chitosan (AESQ741)	1.01	0.76	1.11	1.07	0.61	0.87	1.07	
FWA-tetrasulfonated (BlankPL)	1.00	0.82	1.10	1.06	0.80	1.24	1.04	
FWA-hexasulfonated (BlankUW)	0.97	0.82	1.10	1.07	0.81	1.24	1.02	
FWA-disulfonated (BlankAWP)	1.01	0.81	1.09	1.03	0.78	1.20	1.03	
Carboxymethylcellulose (LT446A)	1.02	0.91	1.09	1.10	0.85	1.13	1.06	
Sodium laurylsulfate	0.95	0.89	1.07	1.01	0.84	1.12	1.00	
Hemicellulose (corn fibre gum)	1.03	0.82	1.06	1.03	0.74	1.08	1.00	
Carboxymethylcellulose (average)	1.03	0.82	1.06	1.02	0.69	1.01	0.98	
Anionic guar (GPX241)	1.10	0.88	1.06	1.15	0.85	1.12	1.03	
Cationic guar (SP813D)	1.03	0.80	0.96	0.98	0.82	1.09	1.03	
Direct Orange (Pont KrOrOCC)	0.84	0.70	0.94	0.98	0.77	1.19	1.01	
Acrylamide copolymer (H2000)	1.03	0.74	0.92	1.09	0.75	1.05	0.97	

As can be seen from Table 4-2, a wide range of chemical additives yielded relative changes in virgin STFI compression strength in the range 0.84 to 1.14. A comparison of the figures in the first and second columns of data shows that the recycled sheets were weaker than the virgin sheets from the same recipe. In

other words, the chemicals listed did not fully prevent strength loss, compared to virgin sheets made from the same chemical-treated pulp. On the other hand, certain chemical treatments did have important relative effects, shown in the third column of data, when comparing the results with recycled sheets made from untreated pulp.

Cursory inspection of the tensile strength data, in comparison to the compression strength data, reveals that the two types of test results did not necessarily respond in the same way to various chemical treatments. To make this contrast more apparent, the STFI compression results corresponding to Table 4-2 were plotted as a function of tensile strength results. Figure 4-9 compares the two types of results in the case of recycled sheets, compared with their respective recycled controls.

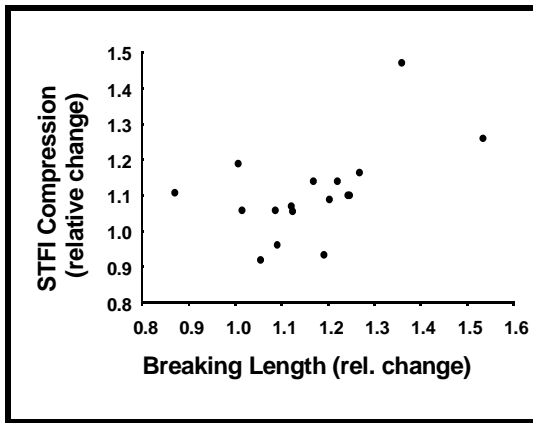


Fig. 4-9. Compression strength vs. tensile strength of recycled handsheets

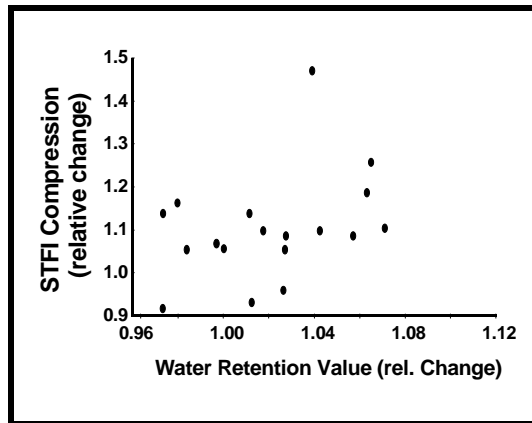


Fig. 4-10. Compression strength of recycled sheets vs. WRV of the recycled fibers

To understand why certain chemicals affected compression strength to a different degree than they affected breaking length, an initial step was to look for trends based on classes of chemical treatments. Treatments favoring recycled STFI strength over recycled tensile strength included the following: chitosan (low-

mass type), anionic starch, oxidized starch, and perhaps cationic starch. Treatments favoring recycled tensile strength over compression strength included direct dye, fluorescent whitening agents (which are chemically related to dyes), an anionic acrylamide copolymer, cationic guar, and hydroxyethyl starch. It is interesting that each of these lists includes some cationic, anionic, and nearly uncharged materials. One difference was that the treatments favoring recycled breaking length over compression strength usually contained hydrophobic chemical groups. By contrast, the treatments most favoring recycled compression strength were hydrophilic polysaccharide products.

As shown in Fig. 4-10 there was no consistent relationship between recycled compression strength and the water retention values of the corresponding recycled pulp, from which the sheets were made. Treatments yielding the highest WRVs of recycled fibers included oxidized starch, chitosan, various other starch products, and a certain carboxymethylcellulose of low charge density (LT446A). Treatments yielding the lowest WRVs of recycled fibers included anionic acrylamide copolymer, certain guar products, most of the CMC products, and an anionic surfactant. An initial hypothesis to explain these results is that the higher values were achieved in cases where there was sufficient driving force to retain a higher amount of water-holding polymeric material at fiber surfaces. This requirement is most easily met in the case of cationic materials including cationic starch and chitosan, and the other materials having similar effects were generally on the low end of charge density. Based on theoretical work by McKenzie [65], one can expect better adhesion between

fibrous surfaces if polymeric chains on those surfaces are capable of mixing within a three-dimensional inter-phase region. It makes sense that cationic starch should give favorable bonding results, since the positively charged groups provide a driving force for mixing with anionic polymers on an adjacent fiber surface. These observations are of a preliminary nature, indicating factors that deserve attention in future work.

There was no correlation between the compression strength of treated virgin handsheets and the recycled sheets made from the same material, after rewetting the initial sheets, dispersal of the fibers, and forming into recycled sheets. One might expect additives to have a similar effect in both virgin and recycled paper. A likely explanation was most clearly stated by Pycraft [8]. His hypothesis states that conditions most favorable to the formation of strong virgin paper from kraft pulps are also most conducive to the loss of bonding potential through such mechanisms as pore closure or hardening of the fiber surface due to crystallization of polysaccharide chains. Also, one cannot rule out effects of detailed chemical differences, the ability of certain chemicals to affect the formation of the virgin handsheets, and random experimental error. The operations of papermaking, conversion, use, and recycling can be expected to degrade polymers and result in unequal yield losses of different paper components. Because cationic starch was a leader for increasing compression strength of both virgin sheets and recycled sheets made from the pre-treated fibers, that chemical deserves more study, regardless of the mechanisms involved.

Results of Tests at Lower Treatment Levels

Low treatment levels make economic sense. An additional motivation here was to be able to test certain chemicals that had undesired effects at 2% addition. For example, attempts to run tests at the 2% level of natural, high-mass guar gum yielded sheets too sticky to be removed from the forming screen of the handsheet mould.

Table 4-3. Relative changes in strength and water retention due to drying, as affected by chemical treatment of the never-dried fiber (lower treatment levels)

Additive	Change Relative to the Control							
	Property:	STFI Compression			Breaking Length			WRV
Sample:	Virgin	Recy.	Recy.	Virgin	Recy.	Recy.	Recy.	
Control:	Virgin	Virgin	Recy.	Virgin	Virgin	Recy.	Recy.	
Level (%)								
UNTREATED	0	1.00	0.78	1.00	1.00	0.69	1.00	1.00
Anionic guar (GPX241)	1	1.13	1.01	1.21	1.04	0.78	1.03	1.05
High-mass chitosan (SC442)	0.5	1.01	0.80	1.16	1.11	0.66	0.95	1.07
Cat. depol. guar (GPX247)	1	0.97	0.93	1.12	1.11	0.84	1.11	0.99
Underivatized guar (SprclU)	1	1.03	0.87	1.07	1.16	0.88	1.23	0.97
Cationic guar (SP813D)	1	1.08	0.78	0.94	1.04	0.84	1.12	1.00
Low-mass poly-DADMAC	1.3	1.04	0.57	0.77	1.05	0.57	0.87	0.97

Results of tests with lower chemical dosages are shown in Table 4-3. With one exception, the relative changes in STFI compression strength were generally similar to those observed with 2% treatment. Effects of chemicals on the compression strength of virgin sheets ranged from positive to near zero. Several of the treatments with guar and chitosan products improved the compression strength of recycled sheets, relative to the recycled controls. However, treatment with 1.3% poly-diallyldimethylammonium chloride (poly-DADMAC) yielded contrasting results; the relative effect on recycled strength was strongly negative,

despite the fact that poly-DADMAC had a positive effect on the strength of the virgin sheets.

A mechanism that may account for the adverse effect of poly-DADMAC on the compression and tensile strength of the recycled sheets involves the ability of such highly charged polyelectrolytes to neutralize the net charge of fiber surfaces. As shown by Lindström and Carlsson [10], kraft fibers that have significant net negative charge at their surface are generally less susceptible to strength loss, compared to those that have a near-neutral charge. Apparently the charged groups either inhibit pore closure or promote rehydration when the paper is rewetted. This explanation is also consistent with the lower value of water retention value in the case of recycled fibers that had been pre-treated with poly-DADMAC.

Effects of Sequential Treatments with Oppositely Charged Additives

Table 4-4 summarizes results of tests involving sequential addition of a cationic additive and an anionic additive. In most tests the cationic material was added first. The combination treatment yielding the largest net gains in both virgin and recycled strength involved chitosan (cationic) and CMC (anionic). The relative effect of the various dual-chemical treatments on compression strength of virgin paper was generally consistent with a linear summation of effects of each additive. For example if one notes that 1.3% low-mass poly-DADMAC (Table 4-3) yielded a relative change of 1.04, and 2% carboxymethylcellulose (CMC) yielded a relative change of 1.03 (Table 4-2), it makes sense to expect a net relative effect of about 1.07 on the compression strength of virgin sheets

following sequential treatment by both chemicals. As shown in Table 4-4, the net effect was 1.10, 1.06, or 1.09, depending on the order of addition and the particular sample of CMC and the amount of poly-DADMAC (not always 1.3%).

Table 4-4. Effects of sequential treatments with oppositely charged polyelectrolytes: relative changes in strength and water retention due to drying

Additives		Change Relative To The Control						
		Property: <u>STFI Compression</u>			Breaking Length		WRV	
		Sample: Virgin	Recy.	Recy.	Virgin	Recy.	Recy.	Recy.
		Control Type: Virgin	Virgin	Recy.	Virgin	Virgin	Recy.	Recy.
First Additive	Second Additive							
UNTREATED		1.00	0.88	1.00	1.00	0.75	1.00	1.00
Chitosan, HM (0.5%)	CMC 7M (2%)	1.04	0.96	1.40	1.25	0.99	1.42	1.10
CMC 7M (2%)	DADMAC, HM (0.5%)	1.10	0.93	1.25	1.14	0.89	1.37	1.07
Chitosan LM (2%)	CMC 7M (2%)	1.05	0.79	1.16	1.07	0.56	0.79	1.08
DADMAC, LM (0.5%)	CMC LT446 (2%)	1.06	0.96	1.15	1.13	0.95	1.26	1.04
DADMAC, LM (1.3%)	CMC 7M (2%)	1.09	0.84	1.14	1.32	1.03	1.59	0.99
DADMAC, LM (1.3%)	FWA-hexa (2%)	0.98	0.84	1.13	1.07	0.77	1.18	0.97

Contrasting results were found when comparing the compression strengths after recycling. Except in the case of chitosan, the results of individual treatments would not have suggested the strengths of recycled sheets in the range 1.13 to 1.40 relative to the recycled, untreated controls. For example, 1.3% poly-DADMAC by itself yielded a change of 0.77 relative to the untreated, recycled control, and 2% CMC yielded a relative change that averaged 1.06. Simple addition of the two effects yields an overall relative change of 0.83. Though more sophisticated mathematical treatments could be considered, the results of such calculations do not explain the actual observed values of 1.14 through 1.25 for the compression strengths of recycled sheets, relative to recycled sheets from untreated fiber.

As described in the Theory section, a mechanism that may better account for the effects of dual treatments is based on polyelectrolyte complexation. In principle, pre-treatment by poly-DADMAC is expected to provide adsorption sites for the water-loving, anionic CMC chains. Alternatively, post-addition of poly-DADMAC, after the CMC, is expected to precipitate a complex of the two polymers onto the fiber surfaces. The latter mode of addition yielded higher recycled strength in the one case where that was tried in Table 4-4. Further work is planned relative to the charge densities and ratios of oppositely charged additives and the relationship between the results and the colloidal charge properties of the furnish.

Results in Table 4-4 for recycled compression strength were very well correlated with the trend in water retention values. Here again, simple addition of the effects of the individual agents does not predict the observed WRV data. Poly-DADMAC at the 1.3% level yielded 0.97 times the WRV value of untreated, recycled pulp (Table 4-3), and the main series of CMC samples at the 2% level yielded 0.98 times the recycled control value (Table 4-2). By contrast, the observed values for combinations of the two polymers (not always at the same dosages) were 0.99 to 1.07, with the higher values at the lower dosage of the cationic polymer. These results suggest that bound water in the adsorbed polyelectrolyte complexes themselves may account for the observed effects on WRV values. This possibility is proposed here as a hypothesis, and a focus of planned follow-up work.

CONCLUSIONS

The answer to the question in the title of this article is “yes”. Several water-soluble materials or sequences of two additives increased the strength of recycled handsheets, compared to recycled control handsheets that had not been treated before their first drying.

Results were consistent with persistence of adhesiveness of surface-bound polyelectrolytes. These materials at the fiber surface contributed to bonding even after the initial paper had been reslurried and formed into second-generation handsheets. However, the positive effects of polymeric pre-treatments on the strength of recycled handsheets did not appear to be related to the water-holding ability of fiber cell walls.

Tensile *versus* compression test results were affected differently by certain chemicals. Treatments favoring compression strength included many water-loving polymers, such as polysaccharide products. Treatments favoring tensile strength included chemicals having hydrophobic substituent groups.

Based on the screening tests reported in this article, the following candidate treatments appeared most promising for maximizing the strength of recycled paper, or reducing the need for additional strength additives when paper is recycled: cationic starch, various other starch products, depolymerized guar products, chitosan, and sequential addition of a cationic material and an anionic polymer such as carboxymethylcellulose (CMC).

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CHAPTER 5

Effects of Sugar Addition Before Drying on the Wet-Flexibility of Redispersed Kraft Fibers

ABSTRACT

Paper made from recycled, chemically pulped fibers typically has lower strength than paper made from virgin fibers. This was confirmed with respect to tensile and compression strength for an unbleached softwood kraft pulp. It was also confirmed that the addition of sucrose, at high concentration, to virgin pulp before drying could improve the recycled paper strength, compared to a control with no sugar added. The use of glucose was found to be slightly more effective than sucrose. Fibers treated with the sugars were found to have higher flexibility and water retention values than untreated fibers that had been subjected to the same drying conditions.

INTRODUCTION

Since the 1960's there has been increasing interest in factors responsible for the loss of inter-fiber bonding ability when chemical pulps, such as kraft or sulfite, are dried and then resuspended in water [1-7]. One explanation for this behavior is that the fibers and fines become less able to swell in water [1, 2, 8-10], a phenomenon often attributed to irreversible closure of micropores in the fiber cell wall [10-13]. Other investigators have considered changes in the wet flexibility of fibers [8, 11, 13]. Fibers with stiffer surfaces would be expected to form less relative bonded area under fixed conditions of wet pressing and drying [15-16]. Recently it has been proposed that some or all of the observed loss in

bonding ability is due to chemical factors at the fiber surfaces [17], possibly involving changes in the ability of surface-bound polymer chains to inter-diffuse [18].

In 1963, Higgins and McKenzie [1] found that a high concentration of sucrose (20% solution by weight) present during drying could reduce the loss of bonding ability when kraft or neutral sulfite pulps were dried. They attributed this effect to the action of sucrose in forming reversible hydrogen bonds with fibers during the drying process. It was proposed that such bonds could be more readily broken on re-wetting than the intra-fiber bonds formed during drying. At that time the concept of fiber pores as described by Stone and Scallan [10,19], using a solute exclusion method, had not yet been published. Modern concepts of cell wall architecture and fiber swelling are to a great extent founded on the results obtained using this technique [20].

Given the known nano-scale pore size distribution of never-dried, unbleached kraft fibers [19, 21-22], relative to the even smaller size of monomeric sugar molecules [19], it is reasonable to expect the sugar molecules to enter the cell wall with a solution and remain there during the evaporative drying of paper. Due to the high water-solubility of sugars and their lack of ionic charge it has been assumed, to a first approximation, that such molecules are neither enriched nor depleted at the wetted fiber surfaces, relative to their bulk concentration [10]. Such an assumption implies that the concentration of sugar in solution that enters the fiber wall ought to be similar to the bulk concentration. The low volatility of sugars, including glucose and sucrose, ensures that the

molecules are left behind when water evaporates. Extending the surface tension mechanism proposed by Campbell [23], the receding films of water within fiber pores during the drying of paper are expected to cause pores in the fiber wall to collapse [24]. Sugar remaining within collapsed pores would be expected to form hydrogen bonds with the adjacent cellulosic materials [23]. The important question then is how the presence of monomeric sugars would affect reopening of the pores when the fibers are reimmersed in water. Despite their chemical similarity with the monomeric sugars, only the cellulose molecules of the cell wall have a known ability to form insoluble crystalline zones due to cooperative hydrogen bonding along their highly regular molecular chains [25-28]. By contrast, monomeric sugars lack the size and regularity required to form insoluble crystallites. The importance of such mechanisms is underscored by observed effects of surface derivatization procedures that interrupt the structure of cellulose chains [29, 30].

Fiber flexibility tests have the potential to provide additional evidence to test the hypothesis that sugars modify the process of fiber-wall pore collapse or make such pores more likely to reopen upon rewetting. A fiber with closed pores is expected to have a stiffer surface, compared to one in which the pores remain more open [31, 32]. Many techniques have been devised to measure wet fiber flexibility [16, 33-39]. Among these, the method of Steadman and Luner [36] appeared especially well suited to the needs of the present study, due to the relative simplicity of the measurement and the fact that the technique measures the wet flexibility of a relatively large number of fibers more quickly and

reproducibly compared with other techniques. Steadman and Luner [36] used this technique to find that there is a linear, but not unique, relationship between sheet apparent density and average wet fiber flexibility for a number of pulps and pulp treatments. Paavilainen and Luner [39] also used the technique to conclude that at least half of the wet fiber flexibility value was lost on air-drying. The goal of the experiments to be described herein was to determine whether the addition of monomeric sugar molecules to never-dried kraft fibers has a significant effect on the wet flexibility after those same fibers have been dried and then resuspended in water.

EXPERIMENTAL

Materials

Pulp: Never-dried, unbleached pine kraft pulp was obtained from the Mansfield, Louisiana mill of International Paper. The sample was taken from the high-density storage, after the pulp had passed through the blowline and de-shive refiners. Upon its receipt from the mill, the pulp was screened and centrifuged to 30% consistency. The fibers were fluffed and then refrigerated during storage. These procedures made it possible to carry out experiments from a highly consistent master batch of fibers. The unrefined pulp had a freeness of approximately 760 ml CSF.

Chemicals: Reagent-grade sucrose (Fisher, Lot.701806) and anhydrous α -D-glucose (Aldrich, catalog number 158968) were used without further purification.

Equipment: Microscopic observations and digital images were obtained with an Olympus BH2-UMA microscope with Sony 3CCD Color Video Camera (Model: DXC-970MD). The images were captured and evaluated using Image-Pro Plus software (Version 4.0, Media Cybermetrics). Micro glass slides (75mm x 50mm x 1mm, Aldrich catalog number Z162698) and stainless steel wire (25.4 μm , Cybermetrics) were used to prepare wired slides for the fiber flexibility tests.

Procedures

Although the procedure for refining pulp and handsheet making were described earlier [40], the detailed procedures for them have been reproduced here because the procedure was modified slightly.

Refining by Valley Beater: Sub-batches of centrifuged pulp were taken from cold storage and refined with a laboratory Hollander-type beater (Valley Machinery, Inc.), following the procedure of TAPPI method T-200. The pulp was dispersed in the beater for 30 minutes (zero load) then refined for 20 minutes. The pulp then was screened, centrifuged to approximately 30% consistency, fluffed, and then refrigerated again until use. The freeness of the pulp refined in this way before making handsheets was approximately 700 ml CSF.

Handsheets: Before making handsheets, the refined pulp was dispersed in a disintegrator for 5 minutes. As shown in Fig. 5-1, the refined pulp was added to either a sugar solution or to dilution water (for control tests). The final concentration of sugar solutions was 2% dry mass on dry mass. The pulp samples were mixed with chemicals for 12 hours with stirring before a pad of fibers was formed on a Büchner apparatus with vacuum applied. In each case,

ten pads were required and each pad weighed around 2.4 grams (O.D.). The pads were dried in a TAPPI standard conditioning room (50.0% ± 2.0% RH and 23.0 ± 1.0 °C) for at least 12 hours before physical properties were tested. For making recycled handsheets, the procedure of TAPPI Standard Method T-205 was used, with the following modifications. Instead of the standard slurry pulp consistency 0.3%, a 0.6% consistency was used. As a result the basis weight of the handsheets was 120 g/m², not 60 g/m². At the higher basis weight the samples are not expected to fail in a "buckling" mode during STFI compression strength tests [41, 42]. Instead, they are expected to fail by the desired shear/internal bond failure.

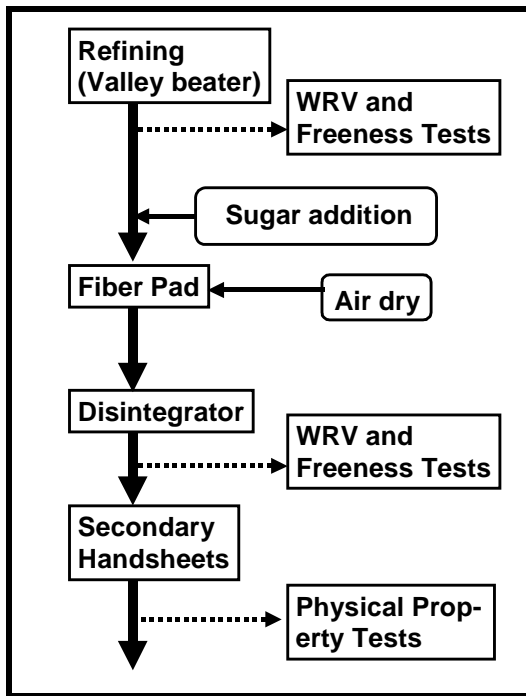


Fig. 5-1. Procedure for handsheets in which virgin pulp was dried in presence of concentrated sugar solution

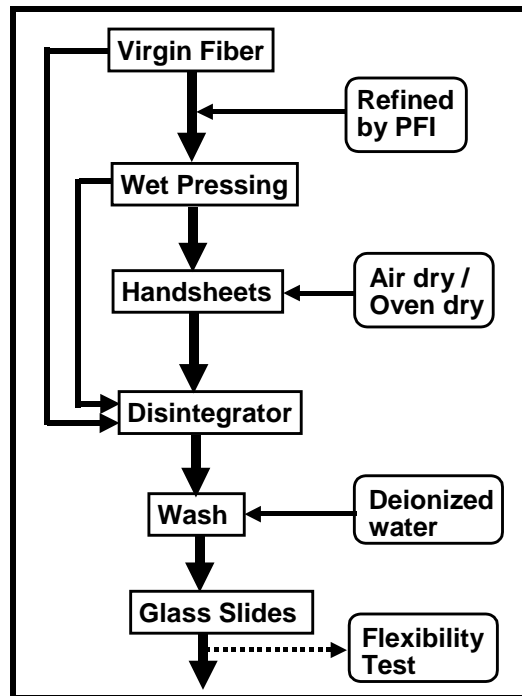


Fig. 5-2. Procedure for the effect of wet press and drying on fiber flexibility

Water Retention Value (WRV): The water retention value (WRV) was used as a measure of the internal fiber swelling capacity of the pulp [43]. The

procedure followed TAPPI test UM 256 with some modifications. Prior to measurement, the pulp was dispersed in a disintegrator for 5 minutes (15,000 revolutions), thoroughly washed in a large excess of de-ionized water, and allowed to stand in water overnight. Following further washing, the pulp was collected on a vacuum filter and dewatered to 25% solids. Moist samples of pulp (equivalent to 0.16 g dry mass) were placed in sintered centrifuge tubes (pore size 0.22 μm , volume 3 ml, provided by MSI). Samples were centrifuged at 900 g for 30 minutes according to TAPPI UM-256. After centrifugation, the moisture content of the samples was determined by weighing immediately and also after drying at 105 °C for 2 hours and cooling in a desiccator jar (anhydrous calcium sulfate) for 30 minutes.

Refining by PFI Mill: As shown in Fig. 5-2, a PFI mill was used to refine the relatively small batches of pulps needed for flexibility analysis. Thirty grams of pulp were taken from cold storage and refined with a PFI mill (9000 revolutions). The procedure for refining pulp by PFI followed TAPPI test T-248. The refined pulp (10% consistency) was put in a zip-lock plastic bag and stored in a cold room for future use. These conditions yielded freeness values of approximately 420 ml CSF.

Fiber Flexibility: In the fiber flexibility test a sparse layer of fibers, mainly lying separate from each other, was formed on the wire of a standard sheet machine. Around 5 ml of pulp slurry (1% consistency) was used to make the fiber layer. The layer was then couched onto a #4 Whatman filter paper using standard sheet technique, corresponding to TAPPI Method T-205. A glass slide

having several thin stainless steel wires (diameter=25 μm) wrapped across its surface in a parallel pattern was laid onto the filter paper. The filter paper and slide were then pressed against each other between two sets of water-saturated blotters in a regular handsheet press. After a two-minute pressing at 50 psi, the glass slides were separated from the blotters and filter paper and viewed in a microscope under incident light. The areas of intimate contact between the fibers and the glass appeared dark, and the area that is not in contact, for instance as the fibers cross over the wire, was less visible. The explanation of the incident light image is based on the theory of thin film interference [44]. It makes sense that the no-contact length is related to the flexibility of the fiber, and as the fiber becomes more flexible this distance will decrease. The detailed procedure for preparing slides appears in the literature [36]. The image analysis software was used to measure the width and less-visible length of the fibers crossing over the wires. Around 100 fibers were chosen for a standard set of flexibility tests.

Preparation of Samples for Fiber Flexibility Determination: In the study of the effects of drying and wet pressing on fiber flexibility of refined pulp, four portions (2.4 grams oven dry each) of the refined pulp were taken from cold storage. Each portion was soaked in deionized water for 2 hours before being dispersed in a disintegrator for 5 minutes. After soaking, different procedures were adopted for specific experiments.

Effects of drying and wet pressing: Further steps in the procedure for determining the effect of drying and wet pressing on fiber flexibility are outlined in Fig. 5-2. In the case of control experiments the fiber slurry was washed in a

large excess of deionized water before standing in deionized water for 4 hours before measurement of fiber flexibility.

To study the effect of wet pressing, fibers soaked in the same way were formed into handsheets, wet pressed using the standard TAPPI pressing method, and then dispersed immediately in a TAPPI disintegrator for 5 minutes. This was followed by another washing in a large excess of deionized water. The washed fiber slurry then was kept in deionized water for an additional 4 hours before performing a fiber flexibility test.

To study effects of oven drying, handsheets were made from dispersed fiber suspensions and dried in an oven for 10 minutes at 105 °C before being put in a TAPPI standard conditioning room for 12 hours. The handsheet was soaked in deionized water for 6 hours before being dispersed in a disintegrator for 5 minutes. Subsequent soaking and flexibility measurement steps were the same as given above. The procedure in the case of air-drying was identical, except that the handsheets were not oven-dried but were put directly in a TAPPI standard conditioning room for 12 hours.

Effects of sugars: To determine the effect of sugars on the flexibility of refined fiber, four 1.2 g amounts (based on O.D.) of the refined pulp were taken from cold storage. The pulp samples were soaked in deionized water for 2 hours before being dispersed in a disintegrator for 5 minutes individually. After that, different procedures were adopted for specific experiments.

In the case of control experiments the fiber slurry was left standing in deionized water for 12 hours before making a fiber pad on a filter paper

(Whatman #4). The fiber pad was dried in a TAPPI standard conditioning room for 12 hours, and then soaked in deionized water for at least 4 hours before being dispersed in a disintegrator for 5 minutes. The slurry was washed in a large excess of deionized water before the fiber flexibility was tested. The water retention value (WRV) was also measured.

To study effects of sucrose and glucose the fiber slurry was combined with a sugar solution and deionized water in order to produce a total volume of one liter having either 2% or 10% sugar by weight in water. The mixture was allowed to soak at room temperature for 12 hours before making a fiber pad on a filter paper (Whatman #4). After that, the procedure was the same as that of the control experiment.

RESULTS AND DISCUSSION

In a previous publication [40] it was shown that the tensile strength and STFI compression strength of recycled handsheets made from unbleached softwood kraft pulp were reduced relative to the corresponding primary handsheets made from virgin fibers. The water retention value decreased as well. According to other results [10], there is irreversible pore closure during recycling, and this is assumed to contribute to the observed strength loss.

Effects of Sugars on Paper Strength

As shown in Fig. 5-3, adding sucrose or glucose to virgin pulp increased the tensile strength and compression strength of recycled handsheets, compared to the control experiments. A t-test showed that the increases in breaking length,

STFI compression and WRV were significant at a 95% confidence level for glucose-treated fiber relative to the control. The relative improvement in strength upon the addition of the sugars before drying is in agreement with the previous findings of Higgins and McKenzie [1]. Further evidence supporting the assumed mechanism of strength loss (pore closure causing increased fiber stiffness) was obtained from the water retention value (WRV) tests. From Fig. 5-3, the WRV of fibers treated with sugars increased compared to the untreated recycled fibers. That is consistent with the explanation that sugars blocked irreversible closure of some pores.

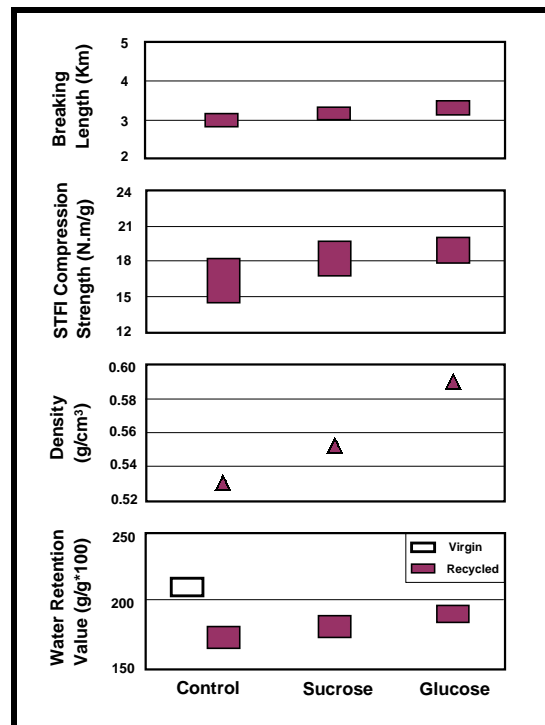


Fig. 5-3. Effect on fiber and paper properties of pretreatment with 2% sugar solutions, followed by drying and resuspension in water (vertical scale of rectangles shows 95% confidence intervals)

According to Fig. 5-3, glucose had a slightly larger effect on breaking length and compression strength, compared to sucrose. Since the molecular weight of

glucose is smaller than that of sucrose, glucose has a better chance to enter smaller pores than sucrose does. This may be one reason why glucose had a higher effect on paper strength than sucrose did. However, the present data are not sufficient to rule out other plausible explanations. For example, the detailed structure of sucrose may be sufficiently different compared to the cellulose chains as to make it less able to adsorb onto fiber surfaces and affect inter-fiber bonding, compared to glucose.

Effect of Drying on Fiber Flexibility

One explanation for reduced bonding ability of recycled kraft pulps has been that pore closure stiffens the fiber, decreases its conformability, and thus results in less fiber-to-fiber bonded area during papermaking [8]. Others have speculated that crystallization also plays a role in this fiber hardening [10,45]. Fiber flexibility tests were carried out to determine whether fiber flexibility correlates with the increased strength and water retention value promoted by sugars.

Though the procedures used for fiber flexibility analysis herein followed the main steps given by Steadman and Luner [36], there were some differences with respect to the calculations. To summarize, the flexibility can be expressed as follows,

$$Fiber\ Flexibility = \frac{1}{EI} = \frac{72d}{PWS^4} \quad (1)$$

where E is the modulus of elasticity (Nm^{-2}), I is the moment of inertia (m^4), d is the wire diameter (m), P is the applied pressure (Pa), W is the projected fiber

width (m), and S is a mathematical estimate of the loaded fiber span (m). A correct form to calculate the loaded fiber span (S) based on the Pythagorean Rule is given by Cresson [46]:

$$S = \sqrt{d^2 + \left(\frac{L}{2}\right)^2} \quad (2)$$

where L is the less-visible length of fiber, as mentioned earlier.

A detailed derivation of equation (1) can be found in the paper of Steadman and Luner [36]. In the present study the geometric mean was used to represent the fiber flexibility of samples instead of the median used by others [35, 36]. This modification of the original approach was justified by the fact that in many cases the maximum values were 1000 times the minimum values. According to Dickey [47] data that is spread over such a wide range is best evaluated by using logarithmic plots and by calculation of geometric means of the logarithms rather than median values. Statistical modeling can be carried out on the log scale to test hypotheses, whereas the distributional results and inferences for medians are not so well developed. For instance, a t-test can be used when determining the effect of sugars on fiber flexibility as long as the distribution of data on the log scale is reasonably close to a normal distribution.

Figure 5-4 shows that wet pressing and drying reduced the flexibility of fibers and that oven drying had the most significant effect on the reduction of fiber flexibility. The limit bars in the figure represent 95% confidence intervals for the mean. The only difference in processing conditions between fibers represented in the two left-most histogram bars was the application of standard pressing, as in TAPPI Method T-205. Though effects of wet-pressing on fiber

properties have been reported by others [48], such effects were not found to be statistically significant in the present study of fiber flexibility. Since the fibers represented in the two right-most bars also had experienced the same wet-pressing operation, it can be argued that they should be compared relative to the “wet-pressing” bar to judge the effect of drying conditions. Only the oven-drying treatment had a significant effect relative to this control at the 95% level of confidence.

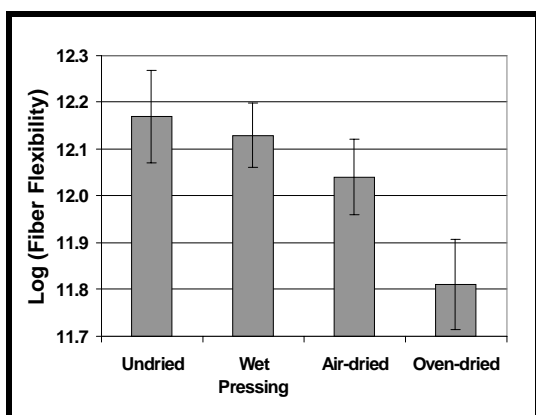


Fig. 5-4. Effect of wet pressing, with or without subsequent drying at either room temperature or 105 °C on the wet-flexibility of refined, soaked unbleached kraft fibers

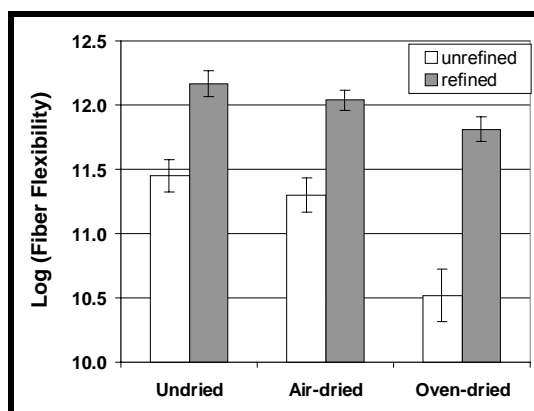


Fig. 5-5. Effect of refining on the flexibility of unbleached kraft fibers under the conditions of never-drying (control), air-drying at room temperature, or oven-drying at 105 °C for 10 minutes

Figure 5-5 shows that the flexibility of unrefined fibers had the same trend as that of refined fibers but that refined fibers were more flexible than unrefined fibers. The freeness of the unrefined fibers was approximately 760 ml, whereas the refined fibers were approximately 420 ml CSF. The results of these flexibility tests are in agreement with observations that paper made from refined fibers has higher relative bonded area and higher paper strength than unrefined fibers. However it is worth noting, in the case of unrefined fibers, that oven-drying had the largest relative effect in terms of the logarithmic scale used for the analysis.

Effect of Sugars on Fiber Flexibility

Results in Fig. 5-6 show that refined fibers treated by sugars before drying were more flexible after drying and reslurrying than untreated refined fibers subjected to the same processing conditions.

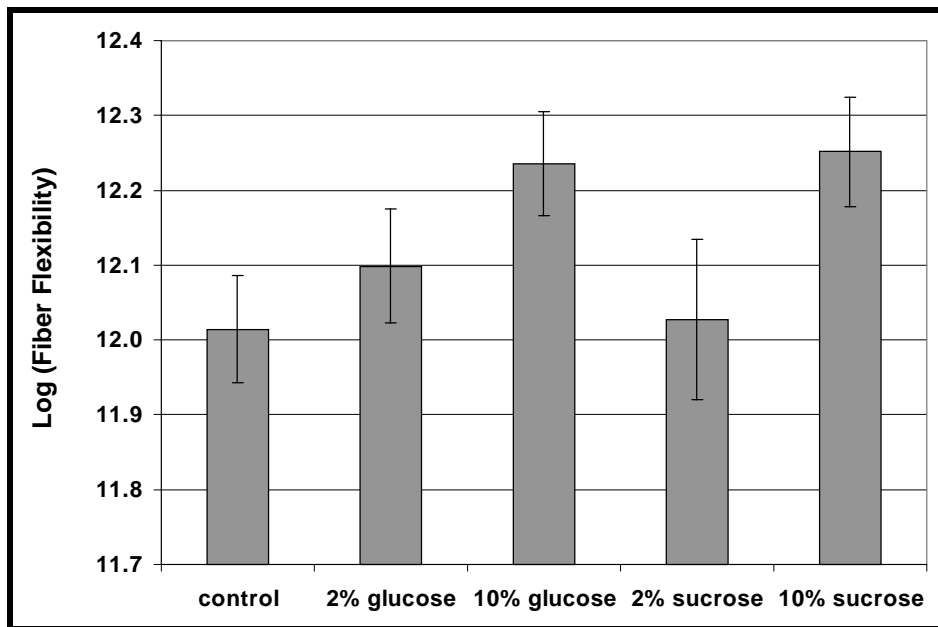


Fig. 5-6. Effect of room temperature drying in the presence of sugar solutions on the flexibility of unbleached kraft fibers after extensive washing and soaking in water

The first histogram bar labeled “control” in this case represents a condition of room temperature drying of fibers collected as a mat on a Büchner apparatus (no pressing). The remaining bars represent the same drying conditions, except that the vacuum-dewatered fiber mats remained permeated with part of the sugar solutions in which they had been suspended. The presence of 10% glucose or sucrose solution at the start of the drying process had a significant effect on fiber flexibility, compared to the control experiment, at a 95% confidence level. The effect of the 2% sugar solutions was not as evident. The fact that a large concentration of sugar was required to achieve a significant effect agreed with

previous work that considered other aspects such as water retention values and inter-fiber bonding [1, 40]. The same fact also is consistent with the earlier assumption that the monomers did not preferentially adsorb to an appreciable extent at the fiber surfaces, relative to their concentration in the adjacent solution.

CONCLUSIONS

The presence of sugars during drying of refined, never-dried kraft fibers improved the strength of the corresponding recycled handsheets, compared to similar samples tested in the absence of sugars. The sugar treatment also caused the water retention values of the recycled fibers to increase relative to an untreated control. For the first time it was shown that sugar-treated fibers showed higher wet-flexibility compared to untreated fibers after drying, extensive rinsing, and soaking. Observed increases in flexibility, WRV and paper strength upon sugar treatments were in agreement with the concept that conformability of fiber surfaces during sheet formation or during subsequent drying play a significant role in determining the strength of inter-fiber bonding.

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CHAPTER 6

Effect of Refining on Changes to Sugar-Treated Kraft Fibers During Recycling

ABSTRACT

Previous results indicated that the addition of sugar to refined, never-dried softwood kraft fibers before drying resulted in improved strength of recycled paper made from the corresponding re-slurried fibers. However, in that study no refining was performed on the recycled fibers. The objective of this study was to determine whether sugar-treatments on virgin fibers enhanced the paper properties of fibers that had been refined during recycling. An unbleached kraft softwood fiber was used for all experiments. Fiber length, fines content, fiber curl and fiber flexibility were measured for fibers with different sugars and refining treatments. Pulp freeness and paper strengths were also measured. It was observed that sugar-treated and untreated pulps had the same recycled strength properties when refining was included in the recycling step. It was also found that refining, when included as a step in recycling, was able to restore the recycled paper to the same strength as paper made from the virgin fibers. Fiber flexibility was decreased upon drying and rewetting. Sugar treatments before drying caused the fiber flexibility to be higher relative to untreated fibers. However, the measured fiber flexibility did not correlate with the recycled paper strength with respect to sugar-treatments. The recycled paper strength depended more on the refining of the recycled pulp than on the addition of sugar to the undried virgin pulp.

INTRODUCTION

Recycled paper made from dried chemical pulp fibers has been shown to have inferior strength compared to paper made from virgin fibers [1-4]. Paper researchers have ascribed this effect to the loss of fiber bonding ability during drying and used a term “hornification” to indicate the change of fibers during drying. The initial definition of the term was related to the loss of water retention value (WRV), which is determined by centrifugation of the fibers to remove external water [5]. Today, people use the term hornification to describe the broad range of physical and chemical changes that occur in pulp fibers during drying. Hornification has been identified with fiber shrinkage and formation of internal hydrogen bonds; a significant portion of these effects is irreversible [6]. It was found that the phenomenon of hornification involves irreversible pore closure in the fiber wall. Whereas some researchers use the WRV as a measure of this effect [7], others [8] prefer to evaluate the fiber saturation point, which involves measuring the swelling of a fiber by a solute exclusion technique [9]. In addition to the simplicity of the method of the WRV test, Robertson considered that using WRV is also closer to the reality of papermaking practice than the method of solute exclusion [10].

Two practical procedures used to improve the strength of recycled paper made from recycled chemical fibers involve either adding dry strength agents to recycled fibers [11] or beating recycled fibers [12] after they are redispersed in water. The drawbacks of these methods include the chemical cost increase and increased energy usage. Also refining fibers results in shorter fibers and

additional fines. These changes bring new problems, such as slower drainage during the formation of the sheet, which may reduce the rate of paper production. It has been proposed that the generation of additional fines results from the recycled fibers being brittle and breaking like matchsticks during refining [12-14].

As described earlier, hornification is believed to occur during the processes of drying fibers. It would be considered desirable if one could reverse the process. One approach to reversing hornification involves mechanical beating, since it has been shown that beating can restore the swelling capacity of hornified fibers [15-16]. Some researchers have disagreed with this approach, saying that beating cannot reverse hornification, based on the idea that hornification is caused by crystallization and that there could be no change in the degree of crystallinity of fibers during beating [17-18]. Another approach involves chemical treatments. It has been noted that mechanical pulps experience less hornification compared to chemical pulps [19]. In that case, lignin and hemicelluloses are embedded between cellulose macromolecules. The higher level of lignin in the high-yield pulp appears to interfere with the formation of inter-hydrogen bonds between microfibrils during drying. Based on this view, some earlier research focused on preventing the formation of new hydrogen bonds or making the new hydrogen bonds broken easily in the processes that follow [20-23].

In light of studies showing the collapse of fiber pores during drying of chemical pulps [8-9], our previous work [24] focused on adding low molecular weight chemicals to virgin pulps. The idea was to prevent pore closure during

drying or to facilitate the opening of pores during rewetting. This method is similar to previous work performed by Higgins in which sucrose or glycerol was added to never-dried fibers, interfering with the formation of hydrogen bonds between microfibrils [23]. However, our research placed greater emphasis on interpreting the results based on changes in microstructure of the fiber wall. Results from our previous work [24] showed that glucose had a more significant effect on WRV in recycled pulps, compared to sucrose. One possible reason is that the lower molecular weight chemical had more chance to enter fiber pores and was then able to remain there during drying. It is reasonable to expect that subsequent rewetting or dispersing may more easily open such pores.

Fiber flexibility tests have the potential to provide direct evidence to support the claim that sugars may modify fiber stiffness and indirectly modify pore collapse. In the past forty years many techniques have been devised to measure wet fiber flexibility [25-32]. Steadman and Luner [32] developed a method to measure flexibility by observing fibers pressed against thin wires. This method was used here due to the relative simplicity of the measurement and the fact that the technique measures the wet flexibility of a relatively large number of fibers more quickly and reproducibly compared with other techniques.

Information related to fines content and fiber length could also provide evidence as to whether the sugar-treated fibers are more flexible than untreated fibers. As mentioned above, recycled kraft fibers tend to be more brittle [12-14], which would be expected to be more susceptible to breakage during beating. After submitting previous work for publication [24], follow-up experiments

revealed a surprising result that the TAPPI disintegrator produced an observable effect on fiber length and fines content. Though the TAPPI disintegrator is not intended to have significant effect on fiber properties, one can imagine that fibers may be cut or some surface material may be removed even by relatively mild mechanical treatments. Results from the work of Heijnesson provided evidence to support this assumption [33]. The author found that the fines content of a fiber slurry increased with increased dispersing time in a disintegrator. In that work, fines were defined as particles passing through a 20 μm sieve. Unfortunately, no information about the effect of a disintegrator on fiber length was reported.

The objective of the present study is to determine the effect of sugar treatment before drying on the response of the fibers to subsequent mechanical actions. It is hypothesized that the sugar treatment will make the fibers more flexible and less susceptible to mechanical degradation on recycling relative to untreated dried fibers. In this study both a gentle mechanical action with a TAPPI disintegrator and a higher energy refining treatments with a PFI mill were utilized.

EXPERIMENTAL

Materials

Pulp: Never-dried, unbleached pine kraft pulp was obtained from the Mansfield, Louisiana mill of International Paper. The sample was obtained from high-density storage after it had passed through the blowline and de-shive refiners. Upon its receipt from the mill the pulp was screened and centrifuged to 30% consistency. The fibers were fluffed and then refrigerated during storage.

Chemicals: Reagent-grade sucrose (Fisher, Lot.701806) and anhydrous α -D-glucose (Aldrich, catalog number 158968) were used to determine the effect of sugars on the recycled refined-fiber properties including fiber length and fine content. Dextrose (D-glucose) anhydrous provided from Fisher (cat. No. D16-3) was used in the set of experiments for determining the effect of PFI refining on the sugar-treated fibers during recycling. All chemicals were used without further purification.

Equipment: Fiber characteristics were evaluated with a Fiber Quality Analyzer (FQA, OpTest Equipment Inc). Microscopic observations and digital images were obtained with an Olympus BH2-UMA microscope with Sony 3CCD Color Video Camera (Model: DXC-970MD). The images were captured and evaluated using Image-Pro Plus (Version 4.0, Media Cybermetrics) with a computer (Windows 98). Also, micro glass slides (75mm x 50mm x 1mm, Fisher catalog number 125535B) and stainless steel wire (25.4 μ m, California Fine Wire Company) were used to prepare wired slides for fiber flexibility tests [32].

Procedures

Effect of Sugar Treatments on PFI Refined Pulp

The procedure for the addition of sugars to the PFI refined pulp is shown in Fig. 6-1. This procedure is similar to that presented in a previous paper [24], with certain additions. Since one purpose of this study was to determine the effect of a disintegrator on sugar-treated fibers during recycling, two extra control experiments were conducted, as shown in Fig. 6-1. One control experiment involved measuring the effect of refining on the physical properties of the never-

dried fibers. Another control experiment involved dispersing a fiber pad collected on a filter paper (Whatman #4), without drying. The third control experiment was carried out on samples without sugar treatment; such experiments involved fiber pad formation and air-drying. All of the tests were carried out with a single batch of thirty grams of pulp taken from cold storage and refined with a PFI mill (9000 revolutions) [34]. Two aspects of the procedure are worth emphasizing: the sugar solutions were added to PFI refined pulp before making fiber pads; and the fiber pads were dried in a TAPPI conditioning room [50.0% ± 2.0% RH and 23.0 ± 1.0 °C] for over 48 hours.

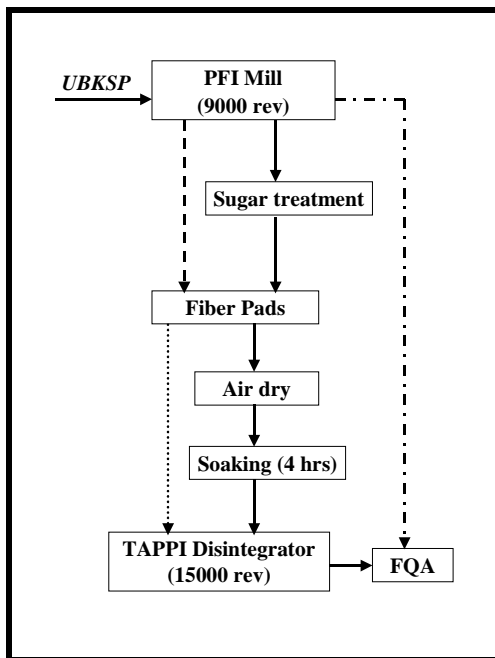


Fig. 6-1. Procedure for the addition of sugars to the PFI refined pulp

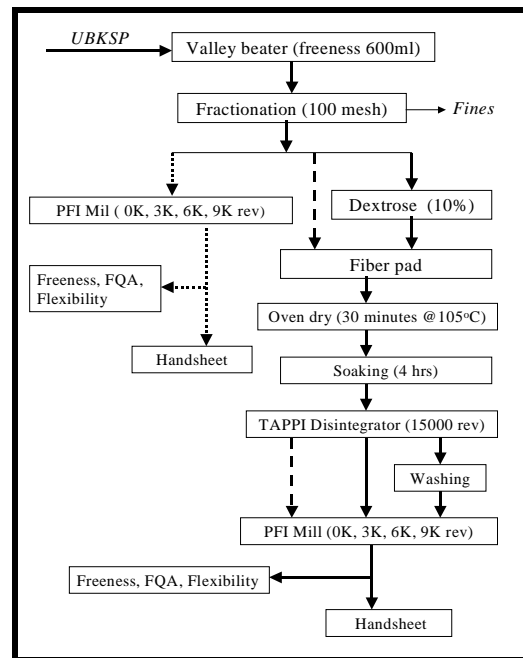


Fig. 6-2. Procedure for the treatment of Dextrose

Effect of Dextrose

Our previous work [24, 35], including the procedure mentioned above, only focused on adding sugar solutions to refined pulps and making handsheets from the recycled fibers without any additional refining. The results from the previous

work [24] showed that sugar-treated virgin fibers that had been dried and rewetted were more flexible, compared to the control experiments, and also that dextrose (D-glucose) had a greater effect on the flexibility of the recycled treated fibers, and on the paper strength of the recycled paper made from the treated fibers. A question was raised: What would happen if dextrose-treated fiber pads were dried and then refined before making handsheets? Another set of experiments was conducted to determine whether treatment by dextrose had an impact on later refining, after the fibers were rewetted. Would the treatment increase recycled paper strength? Or, if the treatment improved the fiber flexibility, would the increased flexibility from dextrose treatment result in less fines generation during refining of the recycled fibers?

As shown in Fig. 6-2, of this study, sub-batches of centrifuged pulp were taken from cold storage and refined with a laboratory Hollander-type beater (Valley Machinery, Inc.), following the procedure of TAPPI method T-200. The pulp was dispersed in the beater for 30 minutes (zero load) then refined for 45 minutes to a freeness of approximately 600 ml. After that, fiber fines were removed via a 100-mesh screen by a Bauer-McNett classifier, following the procedure of TAPPI method T-233. A dextrose solution was added to the fines-free slurry (ca. 0.6% consistency), and then extra water was added in order to reach a final concentration of dextrose of 10% (weight of dextrose to weight of water). The mixture was stirred for 12 hours before making fiber pads on filter paper (Whatman #4). The fiber pads were dried in an oven for 30 minutes at 105 °C and then kept in a TAPPI conditioning room for 48 hours. The dried fiber

pads were soaked for at least 4 hours and then refined by a PFI mill for a specified time (0, 3000, 6000, 9000 revolutions), following TAPPI method T-248, before making handsheets.

Four features of the procedure need to be emphasized. First, in order to amplify the effect of sugar treatment, fibers were refined by the valley beater. This was done because refining can be expected to open up fiber pores, possibly allowing more sugar molecules to enter and remain in the pores during drying. Second, in order to determine the exact amount of the fines generated during PFI refining, the primary fines were removed by 100-mesh screen of a Bauer-McNett classifier. Third, in order to maximize the effect of drying on fiber properties, thirty-minute oven-drying at 105 °C was adopted, relative to overnight air drying in the previous work [24]. Last, the effect of washing on the dextrose-treated and dried fibers before refining was also considered, as shown in Fig. 6-2. In this case, the fiber slurry was washed by a large excess of deionized water.

It should be noted that in this study the basis weight of the handsheets was 120 g/m², not 60 g/m², which is specified in the TAPPI Method. Also the handsheets were kept in a TAPPI conditioning room for 48 hours before paper physical properties tests. At the higher basis weight the samples are not expected to fail in a "buckling" mode during STFI compression strength tests [36, 37]. Instead, they are expected to fail by the desired shear/internal bond failure.

Fiber Flexibility

Before measuring fiber flexibility, the pulp slurry was washed thoroughly with excess deionized water and then kept in deionized water overnight. In the

fiber flexibility test a thin, tangentially-oriented fiber network is formed on the wire of a standard handsheet apparatus. Around 5 ml of pulp slurry (1% consistency) is used to make the fiber network. The network is then couched onto a #4 Whatman filter paper, using the standard sheet forming technique corresponding to TAPPI Method T-205. A glass slide having several thin stainless steel wires ($\varnothing=25\ \mu\text{m}$) attached across its surface in the form of a parallel grid is laid onto the filter paper. The filter paper and slide are then pressed against each other between two sets of water-saturated blotters in a regular handsheet press. After a two-minute pressing at 50 psi, the glass slides are separated from the blotters and filter papers. The fibers adhere to the slide and are viewed in a microscope under incident light. The areas of intimate contact between the fibers and the glass appear dark, and the areas that are not in contact, for instance, as the fibers cross over the wire, are less visible. The explanation of the incident light image is based on the theory of thin film interference [38]. It makes sense that the no-contact length is related to the flexibility of the fiber, and as the fiber becomes more flexible, this distance will decrease. The detailed procedure for preparing slides appears in the literature [32].

Images were captured by a camera attached to a microscope. Image analysis software (Image-Pro Plus 4.0) was used on the digital images to measure the fiber widths and the lengths of the less-visible sections of the fibers crossing over the wires. Around 400~600 fibers were chosen for each experimental condition during standard flexibility testing.

Figure 6-3 shows a schematic of the components used for the fiber flexibility test. Figure 6-4 shows an enlarged picture of a fiber crossing over a wire. Image analysis software was used to capture the pictures and measure the width and the less-visible length (L) of the fibers.

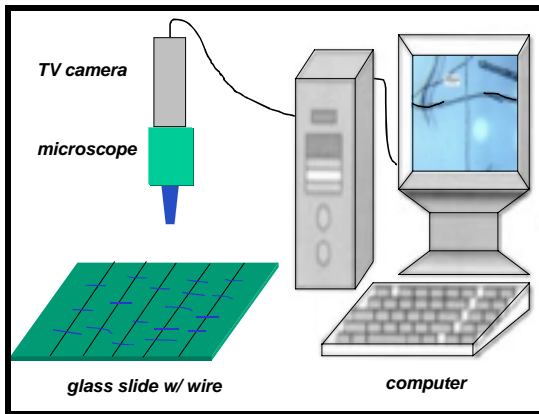


Fig. 6-3. Schematic diagram of flexibility setup.

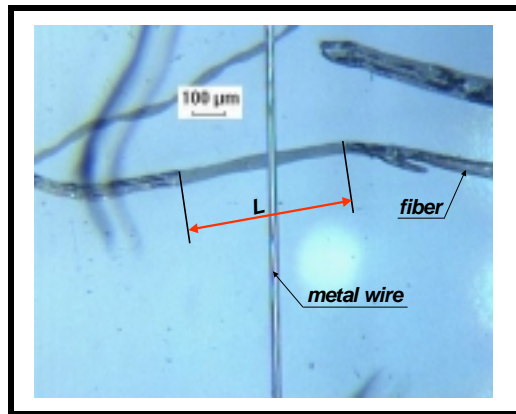


Fig. 6-4. Enlarged picture of a fiber under microscope.

The flexibility can be expressed as follows:

$$\text{Fiber Flexibility} = \frac{1}{EI} = \frac{72d}{PWS^4} \quad (1)$$

Where:

E: modulus of elasticity, $N \cdot m^{-2}$

I: moment of inertia, m^4

d: wire diameter, m

P: pressing pressure, $N \cdot m^{-2}$

W: projected fiber width, m

S: a mathematical estimate of the loaded fiber span, m

A correct form to calculate the loaded fiber span (S) based on the Pythagorean Rule is given by Cresson [39]:

$$S = \sqrt{d^2 + \left(\frac{L}{2}\right)^2} \quad (2)$$

Where:

d: wire diameter, *m*

L: less-visible length, *m*

S: a mathematical estimate of the loaded fiber span, *m*

The detailed derivation of equation (1) can be found in a paper of Steadman and Luner [32]. In the present study the geometric mean was used to represent the fiber flexibility of samples instead of the median used by Steadman and other researchers [28, 30, 32]. Since the maximum may be 1000 times the minimum in the data, according to Dickey [40] when the data is in such a range, a good approach is to analyze the results using logarithmic plots. He suggested reporting the geometric mean, which is somewhat like the median. Researchers are able to perform statistical modeling on the log scale and test hypotheses, whereas the distributional results and inferences for medians are not so well developed. In this study, a t-test can be used when determining the effect of sugars on fiber flexibility because the distribution of data on the log scale fits a normal distribution.

RESULTS AND DISCUSSION

Effects of Sugars on Fiber Physical Properties

Our previous papers [24, 35] showed that sugars applied to virgin pulp before drying could reduce the strength loss of recycled paper and that the treated fibers had higher flexibility than untreated fibers after drying under

matched conditions. This observation raised the following question: Would the increased flexibility resulting from the sugar treatments affect the fiber physical properties during the process of dispersing in a TAPPI disintegrator before making recycled handsheets? Although the TAPPI disintegrator was designed to avoid significant refining action, we hypothesized that the disintegrator may shorten fibers, especially if the fibers had become stiffer as a consequence of drying and recycling. In this study, fiber length and fines content were measured by the Fiber Quality Analyzer (FQA) [41-44].

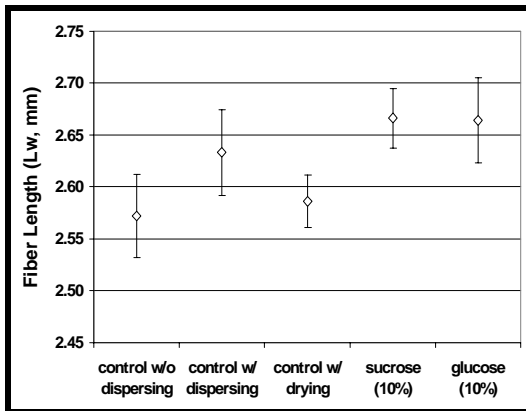


Fig. 6-5. Effect of sugar treatment on refined fibers after recycling. The average and the 95% confidence level are shown.

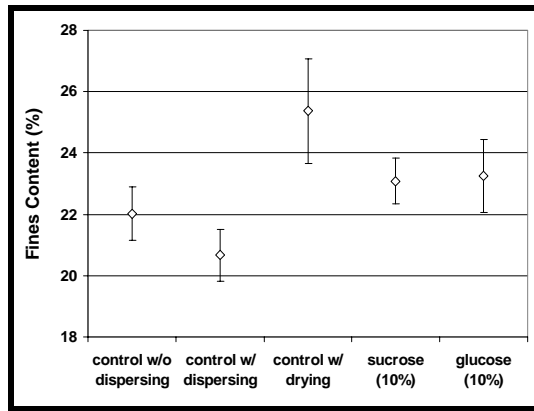


Fig. 6-6. Effect of sugar treatment on refined fibers after recycling. The average and the 95% confidence level are shown.

Figures 6-5 and 6-6 show that the slurry of fibers that had been treated by sugar solutions before drying had fewer fines and slightly longer length compared to the control experiment. These data are the combined results of two replicate experiments. The observations were consistent with the proposal that a less stiff fiber ought to be less susceptible to damage during mechanical action. As shown, there were no significant differences between the two sugar treatments, neither with respect to fiber length nor fines content.

Further explanation may be needed regarding the observed increase in fiber length of the control with dispersing relative to the control without dispersing. It is possible that the difference in fiber curl between these two treatments affected the fiber length measurements. The curl value for the control experiment with dispersing was 0.08, and the curl value of control without dispersing was 0.06 shown in Fig. 6-7. Although the FQA is designed to measure the actual fiber length along the fiber contour, still it is reasonable to expect that the FQA analysis of fiber length may be affected by differences in curl. It is noted that results from Fig. 6-7 indicated that the sugar treatments decreased fiber curl during drying.

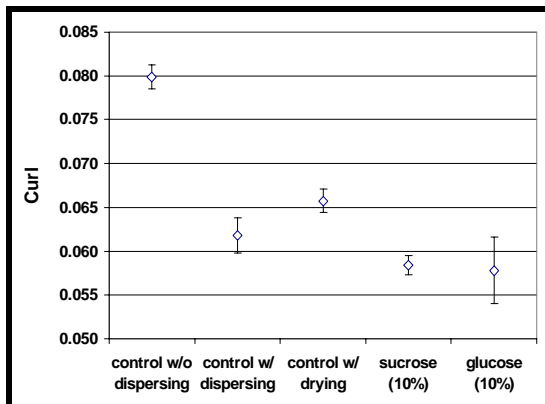


Fig. 6-7. Effect of sugar treatment on refined fibers after recycling. The average and the 95% confidence level are shown.

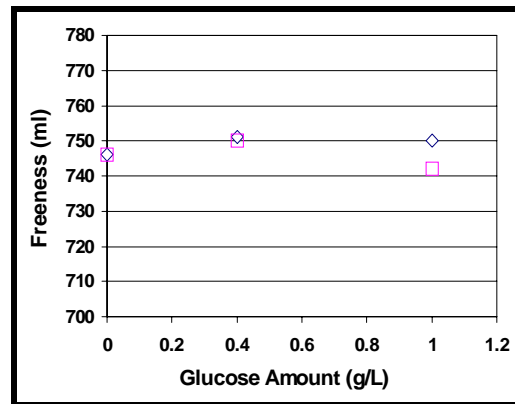


Fig. 6-8. Effect of sugar concentration on the freeness test

A recent article described issues related to the measurement of fines by optical fiber length analyzers [45]. These optical analyzers [40, 46], which use polarized light, can detect the presence of a wood particle, because the cellulose is birefringent. Lignin or particles that contain less cellulose than fibers is not detectable [47]. Furthermore, the author considered that the fines content expressed as percentage is not meaningful either, since pulp fibers are reported

in the literature usually by weight and seldom by number. To obtain more reliable information about fines content it was recommended [45] to use traditional methods [48, 49]. In the traditional method, percent fines are expressed as the ratio of the dry mass of particles passing through 200-mesh screen to the dry mass of the original sample. Nevertheless, our present study still used a count of particles within the range of 0.07 mm to 0.2 mm as the fines percent because the data of fiber length seemed to be inversely proportional to the fines content. Thus the fines content was used as additional support for the fiber length data.

Effect of PFI Refining on the Physical Properties of Dextrose-treated Fibers

The freeness test is sensitive to the fines content of a fiber slurry [50]. If a certain treatment reduces the generation of fiber fines during refining, then it is expected that the treated pulp should have a higher freeness value. In order to exclude the effect of the viscosity of sugar solution on the freeness test results, a preliminary experiment was conducted under different levels of glucose concentrations within the reasonable range. It was found that there was no difference in measured freeness among these different concentrations of glucose, as shown in Fig. 6-8. This result is important because the change of freeness value can be ascribed to the change of fines content only if one can exclude the possible effect of a change in solution viscosity.

Although fiber fibrillation also affects freeness, we did not expect that sugar added to a refined pulp before the freeness test would affect fibrillation. Figure 6-

9 shows that there was no significant difference for freeness among the treatments without any refining or at the mild level of refining.

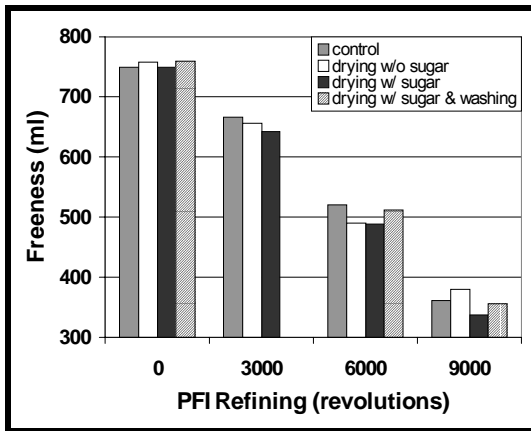


Fig. 6-9. Effect of dextrose treatment on freeness during PFI refining

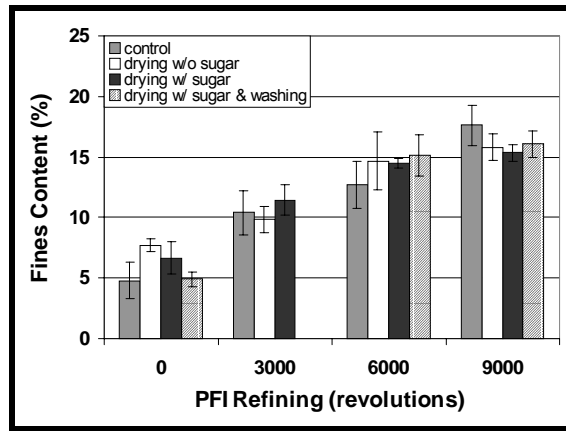


Fig. 6-10. Effect of dextrose treatment on the fine generation during PFI refining

The results in Figs. 6-9 through 6-11 indicate that the effect of refining dominates the properties of the fibers at high levels of refining, masking any effect of the sugar treatment. With no refining, the sugar-treated fibers show lower fines content and higher fiber length in agreement with the data from Figs. 6-5 and 6-6.

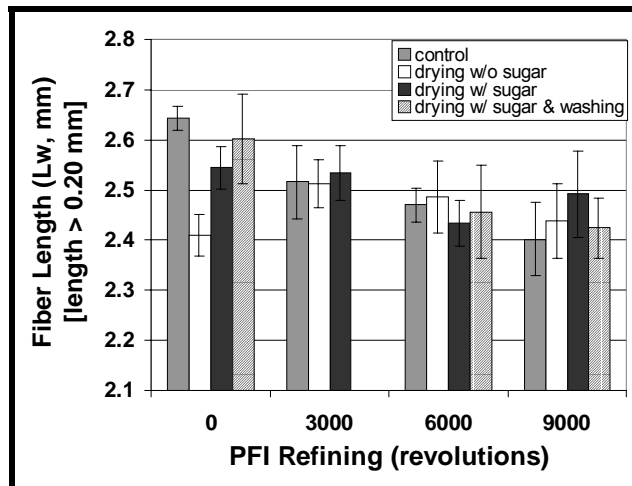


Fig. 6-11. Effect of dextrose treatment on fiber length during PFI refining

Effect of Dextrose-Treatments on Fiber Flexibility

It is of interest to know the effect of the test procedures, including refining, on the fiber flexibility. Our previous work [24], in which refining was applied to the fibers only before drying, showed that refined fibers were more flexible than unrefined fibers, and never-dried fibers were more flexible than dried fibers. In the present study, fibers with 6000 revolutions of PFI refining after drying were chosen to observe such effects.

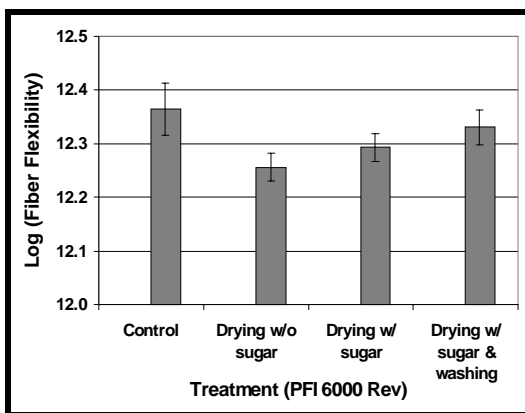


Fig. 6-12. Effect of dextrose on fiber flexibility

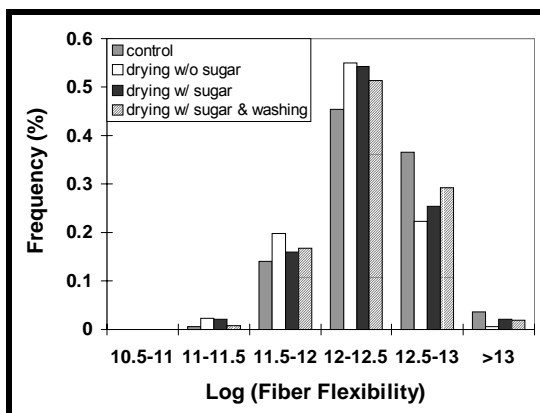


Fig. 6-13. Effect of dextrose on fiber flexibility distribution

Figure 6-12 shows that sugar-treated (dextrose) fibers maintained higher flexibility, compared to untreated fibers that were dried in parallel tests. The error bar shows a 95% confidence level. A t-test showed that there is a significant difference on fiber flexibility between the samples untreated and treated with sugar at a 95% confidence level. Also a t-test showed that the washing process for the samples that had been sugar-treated had a significant effect on fiber flexibility at a 90% confidence level. One possible reason is that removal of sugar from the fiber wall may facilitate fiber lamellas more easily slipping relative to each other during refining. So far there is no specific evidence to support such

an explanation. Again it is noted that dried fiber has lower flexibility compared to a control experiment that did not involve drying.

The distributions of fiber flexibility measured in this study are shown in Fig. 6-13. It can be observed for all samples that there is an approximately normal distribution of fiber flexibility when plotted on a logarithmic scale as expected [40]. More sugar-treated fibers fall within the range of higher flexibility (greater than log fiber flexibility of 12.5) compared to the untreated fibers under similar drying conditions. In accordance, less sugar-treated fibers fall within the range of lower flexibility (less than log fiber flexibility of 12.5) compared to the untreated fibers under similar drying conditions.

Effect of PFI Refining on Recycled Paper Made from Dextrose-treated Fibers

As described in an earlier article [24], paper made from recycled fibers that had been sugar-treated before drying, but without any additional refining treatment, had higher strength (tensile strength and STFI compression strength), compared to paper made from recycled untreated fibers. This is confirmed in Figs. 6-14 and 6-15 for zero PFI revolutions data.

In the present study additional refining was applied before making recycled handsheets. The results in Figs. 6-14 and 6-15 for all levels of PFI refining demonstrate that the application of refining energy eliminated any significant effect of sugar treatment. In fact, the refining was observed to produce strengths almost equivalent to the virgin pulp for all refining levels. This is in agreement

with many studies that have shown that refining could restore fiber swelling to the never-dried level [8, 15, 51].

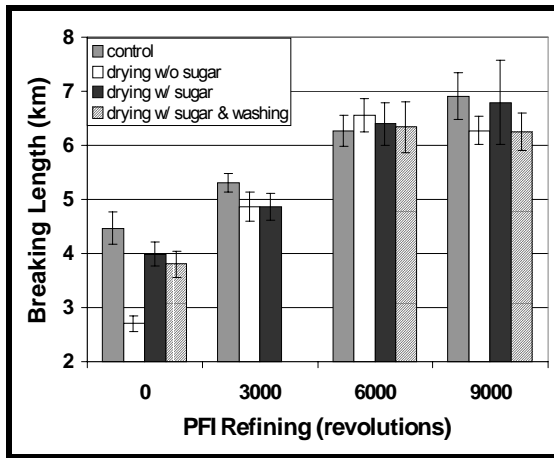


Fig. 6-14. Effect of PFI refining on the tensile strength of recycled paper

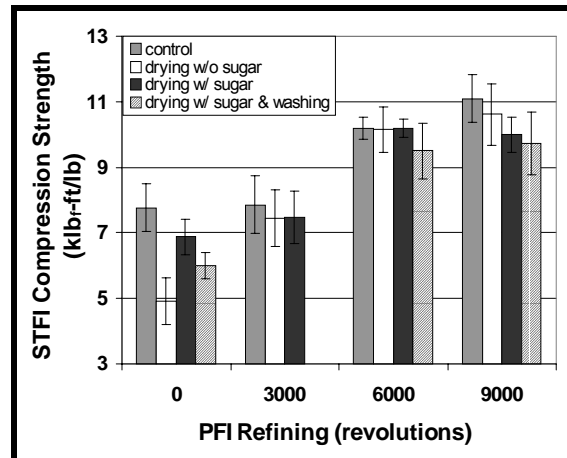


Fig. 6-15. Effect of PFI refining on the compression strength of recycled paper

It is worth paying some attention to paper strength at the refining level of 6000 revolutions, since there are data for the fiber flexibility at that condition, shown in Fig. 6-12. Sugar-treated fibers still showed higher flexibility compared to untreated fibers, even after PFI refining. This was not expected, based on our previous results showing a correlation between the paper strength properties and fiber flexibility for recycled papers with no post-refining [24]. In that previous work, we concluded that paper made from more flexible fibers resulted in greater strength compared to paper made from fibers having lower relative flexibility. It appears that the measured differences in fiber flexibility of our samples was not a dominant factor governing final paper strength in cases where there was additional refining after drying. The process of refining increases external fibrillation. External fibrillation enhances sheet consolidation by entanglements of microfibrils during papermaking and this enhances inter-fiber bonding [52]. Compared to the change in external fibrillation, the change in fiber flexibility

contribution to the bonding between fibers may be less significant, based on the present results.

Although the present results show that refining is a much more dominant effect than sugar treatment and can obscure the effects of previous drying history on paper strength, it is worth bearing in mind that refining is not always an attractive option; refining can cause other problems such as low freeness or excessive fines.

CONCLUSIONS

1. For an unbleached kraft softwood pulp, the TAPPI disintegration process produced small, but statistically significant increases in the average fiber length in recycled pulp and decreases in curl. The TAPPI disintegration process increased the fines content of recycled fibers by no more 2 percent by count.

2. Sugar treatments added to the virgin fibers before initial drying produced recycled paper that was stronger than for untreated fibers in cases where the recycled fibers were not further refined, confirming previous results. However, the treated and untreated pulps had the same increased recycled strength properties when refining was included in the recycling step.

3. Refining during recycling was able to restore the recycled paper to the same strength as paper made from the virgin fibers. No significant difference on freeness was found between refined virgin fibers and refined recycled fibers at the same refining levels.

4. Fiber flexibility was decreased upon drying and rewetting. Sugar treatments before drying caused the fiber flexibility to be higher relative to untreated fibers, even after refining.

5. The measured fiber flexibility did not correlate with the recycled paper strength in the case of refining during recycling.

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CHAPTER 7

The Effect of pH, Electrolyte Concentration and Hardness on Bonding Properties of Unbleached Kraft Fibers

ABSTRACT

Increasing the relative bonded area (RBA) of fibers is one of the main approaches to improve paper strength. Adding dry strength agents or extending refining is a common practical approach to gain strength, and some of this gain has been attributed to increased RBA. It often has been assumed that paper made under alkaline conditions has a strength advantage compared to paper made under acidic conditions. This effect was ascribed to fibers becoming more flexible under alkaline conditions, resulting in increased fiber-fiber bonded area. However, no individual fiber flexibility test was done before to demonstrate this explanation. Researchers have determined the fiber flexibility based on the measurement of water retention value.

In the present study fiber flexibility measurements were carried out in conjunction with strength tests under different conditions of pH. Results showed that no significant effect on the paper strength was found in the range of sheet forming pH from 3 to 8 under typical papermaking conditions, although fiber flexibility tests showed that the unbleached kraft fibers treated under alkaline conditions were more flexible than fibers treated under acid conditions. Neither cellulose molecular mass nor water retention value was affected to a significant extent by the value of pH prior to drying, within the range of 3 to 8. Also the

effects of electrolyte concentration and hardness of fiber slurry on fiber flexibility were investigated.

INTRODUCTION

The aqueous environment of papermaking is critical to the physical properties and end-uses of paper products. The pH value and salt concentration during beating and sheet forming affect the physical properties [1]. It was found that pH is an important variable during refining [2-6]. Different pulps have shown different effects of pH during beating on paper strength [5]; for instance, straw pulp showed minimum strength in the range of pH 7.0 to 7.5, cotton pulp showed a greater strength at pH 8.5, and wood pulps showed the maximum strength at relatively high pH values. Jayme and Büttel [2, 3] found that maximum paper strength was obtained when the wood pulps were refined within the range of pH 10.4 to 11.35, independent of wood pulp species. Lindström and Kolman [1] showed that paper strength increased with the increase of pH during beating and reached a maximum at the pH 11 if the paper was made in deionized water. Bryson [6] found that paper showed higher burst strength when the pulp was refined in an alkaline medium, compared in an acidic medium, but no information about the pulp was mentioned. Chen and Scott [4] found that refining pH had a significant effect on paper strength for bleached pulp in unfilled furnishes, but no effect in the presence of filler.

Acidic conditions of papermaking have been very common, especially during the previous century, due to the prevalence of rosin sizing with alum. It is known that paper made under acidic conditions will become yellow and brittle

during storage, an effect that is regarded as a disaster by archivists and librarians [7]. Studies showed that cellulose hydrolysis was responsible for these effects and that the sheet acidity accelerated the reaction [8-9]. Acidic hydrolysis breaks the linkage of glucose units in the cellulose chain. This reaction shortens and weakens the chain. In principle such breakage is expected to reduce the paper strength, though more work is needed to determine how much hydrolysis has to occur before the effect on paper strength becomes significant. It was found that the alkaline papermaking conditions, using synthetic sizing agents, could avoid paper becoming brittle and yellowing [7]. In addition to affecting the permanence, defined as the extent to which a paper will retain its original properties upon storage, papermakers also have found that the benefits of alkaline papermaking include utilization calcium carbonate, reduced energy consumption, reduced effluent loads, improved productivity, improved sizing, and less corrosion [7, 10, 11]. Although it has been stated that paper made under alkaline conditions is stronger than paper made under acid conditions [1-3, 5, 6, 9-11], the evidence to support this assertion is unclear. If one read these articles carefully, it can be shown that much of the effect of pH on paper strength came from beating pH, not from sheet forming pH [5, 6, 9-11]. Jayme and Büttel [2, 3] found that the largest gains in paper strength were obtained when the pulp was beaten at alkaline conditions and paper formed also at alkaline condition. Lindström and Kolman [1] also found that tensile index of paper made from unbleached kraft pulp increased with pH during sheet forming. It is noted that the pulps from the work of Jayme *et al.* [2, 3] and Lindström *et al.* [1] were highly

washed and soaked at a certain pH condition for 24 hours. Chen and Scott [4] found that the forming pH did not have significant effect on paper strength in the case of bleached kraft fibers.

It is well known that sodium hydroxide can play a useful role during recycling, especially with respect to de-inking. Results [12] have shown that strength of recycled paper increased, compared to a control experiment without the addition of sodium hydroxide. The same author concluded that sodium hydroxide restored the bonding potential either by removing the contaminants from fiber surface or by chemically restoring the bonding potential of fibers. Gurnagul [13] found that the adding sodium hydroxide during repulping sheets made from thermomechanical pulp increased fiber swelling and recycled paper strength, but there was no effect on paper made from unbeaten kraft pulps. Also Lindström and Carlsson [14] found that rewetting pH had significant effect on the strength of secondary paper made from unbleached sulfate pulp. With the increase of rewetting pH, the tensile strength of recycled paper increased. Bovin *et al.* [15] showed that breaking length improved at a constant freeness value if a kraft pulp was disintegrated in an alkaline suspension.

When attempting to explain various effects of pH on paper strength, it has been well established that tensile strength of paper is correlated to fiber swelling [16-18], as indicated by water retention value (WRV) tests [19]. In related work, researchers have found that fiber swelling also depends on pH [1-3, 12]. It was found that the WRV increased with increasing pH up to a maximum value. After that point the WRV decreased with higher pH. Lindström *et al.* [1, 14] found that

such a swelling vs. pH relationship was valid only for unbleached sulfate pulp, not for bleached sulfate pulp. By contrast, Jayme and Büttel [2, 3] found such a relationship for both bleached and unbleached pulp.

To explain the effect of pH it is reasonable to expect that the increased WRV corresponds to increased dissociation of acidic groups within the fiber wall. There are two theories related to fiber swelling [20], both involving acidic groups. One is related to electrostatic interaction. It has been proposed that electrostatic repulsion between microfibrils covered by acidic groups contributes to the expansion of fiber wall [21]. In the case of kraft pulp, most of those groups are carboxyl groups. With the increase of pH value, the degree of dissociation of carboxyl groups increases, which increases the repulsive force. After reaching the maximum swelling at a certain pH value, the degree of swelling decreases with the increase of pH. This is considered to be a shielding effect of the electrostatic forces due to the increased ion concentration. Sodium hydroxide dissociates into two monovalent ions. The monovalent ions increasingly shield charged groups and reduce the repulsive force. From this standpoint fibers show typical polyelectrolyte swelling behavior [22].

The other theory about fiber swelling is based on the Donnan equilibrium [23]. The swelling of cellulose gel is considered to be caused by osmotic pressure differential resulting from a difference in concentration of mobile ions between the interior of the gel and exterior solution. Grignon and Scallan [24] applied Donnan theory to wood fibers and calculated the difference in the concentration of mobile ions within the fiber wall and that in the liquor outside the

wall in the range of papermaking pH. The water is drawn into the fiber wall due to higher concentrations of mobile ions within the wall. The effect was attributed to the acidic groups attached to the fiber wall. When these groups were ionized, the counter-ions of these groups, although mobile, must remain within the wall to maintain electrical neutrality. The authors found [24-26] that the difference in the concentration of mobile ions between within the wall and outside the wall increased initially, reached a maximum, and then decreased with the increase of pH values. Also addition of salt in the fiber slurry reduced the difference at all pH values. According to Donnan theory, the outside cell wall had higher concentration of added salt than the interior when the salt was added to the system.

One objective of the present study is to observe the effect of pH on the strength of paper made from unbleached pine kraft fiber at typical papermaking conditions. It is assumed that fiber flexibility is related to fiber swelling [27-28]. Fibers may become more or less flexible with the change of papermaking conditions [29]. Increased fiber flexibility results in increased fiber-fiber bonded area, and thus improves paper strength. However, researchers usually have relied on water retention values as a means of judging whether fibers become flexible or not. A fiber flexibility test can provide direct evidence to test whether there is a correlation between the flexibility of wet fibers and paper strength. In the past forty years many techniques have been devised to measure wet fiber flexibility [30-37]. Steadman and Luner [37] developed a method to measure flexibility by observing fibers pressed against thin wires in the damp state and

then dried. This method is used here due to the relative simplicity of the measurement and the fact that the technique measures the wet flexibility of a relatively large number of fibers more quickly and reproducibly compared with other techniques. Several different kinds of wood fiber were investigated by means of this technique [37]. However, there is no published information available about fiber flexibility for different papermaking conditions, including factors of pH, salt conductivity and hardness. It is known that cations [17, 38-39] and electrolyte concentration [1, 24, 39-41] affect pulp drainage [38], fiber swelling [1, 17, 24], chemical adsorption [39-41] and paper strength [1, 17]. It is assumed that these factors also affect the fiber flexibility. Therefore, it is also of interest to know the effects of hardness and salt concentration, as well as pH on wet fiber flexibility in this research.

EXPERIMENTAL

Materials

Pulp: Never-dried, unbleached pine kraft pulp was obtained from the Mansfield, Louisiana mill of International Paper. The sample was obtained from high-density storage after it had passed through the blowline and de-shive refiners. Upon its receipt from the mill the pulp was screened and centrifuged to 30% consistency. The fibers were fluffed and then refrigerated during storage. These procedures made it possible to carry out experiments from a highly consistent master batch of fibers.

Chemicals: 0.25N sodium hydroxide (NaOH) and 4N sulfuric acid (H₂SO₄) were used to adjust pH of pulp slurry. 2% concentration sodium sulfate (Na₂SO₄)

was used to adjust salt concentration of pulp slurry. Calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, Fisher) was used to adjust hardness of pulp slurry.

Equipment: Microscopic observations and digital images were obtained with an Olympus BH2-UMA microscope with Sony 3CCD Color Video Camera (Model: DXC-970MD). The images were captured and evaluated with a computer (Windows 98) with analysis software of Image-Pro Plus (Version 4.0, Media Cybermetrics). Potentiometric measurements were obtained with a Model 215 pH meter from Denver Instruments. The conductivity meter used in the experiments was Model 150 from ORION. Micro glass slides (75mm x 50mm x 1mm, Aldrich) and stainless steel wire (25.4 μm , California Fine Wire Company) were used to prepare wired slides for the fiber flexibility test. A Seward laboratory blender (Stomacher 80, Brinkmann) and a constant temperature bath (Model M-1, Cannon Instrument Company) were used to measure cellulose viscosity.

Procedure

Handsheets

From the results of a beater curve with a PFI mill, 9000 revolutions PFI refining was chosen as a control level for the experiments in this series of tests. Four different pH values were selected as conditions of handsheets making in this work: pH 3, pH 4.5, pH 6 and pH 8. A pH of 3 was selected to evaluate what happens when the pulp is essentially fully protonated. A pH of 4.5 represents a case of strongly acidic papermaking. A pH of 6 is more typical of linerboard

production, especially if it involves waste furnish. A pH of 8 represents a fully alkaline papermaking condition.

The procedure for making handsheets was modified slightly from the TAPPI Standard Method T-205: A basis weight of 120 g/m² was used to better represent paperboard properties and to ensure the validity of STFI compression tests; at the higher basis weight the samples are not expected to fail in a "buckling" mode during STFI compression strength tests [42-43]. Instead, they are expected to fail by the desired shear/internal bond failure. Water for making handsheets and pulp slurries both were pre-adjusted to the pre-selected pH values before making handsheets. In this work, sulfuric acid (H₂SO₄) and sodium hydroxide (NaOH) were used to adjust pH values.

All recycled handsheets were formed at pH 6 without extra refining. As in the case of making virgin handsheets (pH=6 condition), all recycled pulp and water for making handsheets were already adjusted to pH 6 before making handsheets. Paper physical tests were carried out after the handsheets were dried in an oven at 105 degrees centigrade for 8 minutes before putting them in the TAPPI standard conditioning room over night.

Water Retention Value (WRV)

The water retention value (WRV) is an important index in this experiment, because WRV measures the internal fiber swelling capacity. The higher the value, the larger is the swelling capacity. The procedure followed TAPPI test UM 256 with some modifications. Prior to measurement, the pulp was dispersed in a disintegrator for 5 minutes (15,000 revolutions), thoroughly washed in a large

excess of de-ionized water, and allowed to stand in water overnight. Following further washing, the pulp was collected on a vacuum filter and dewatered to 20% solids. Moist samples of pulp (equivalent to 0.16 g dry mass) were placed in sintered centrifuge tubes (pore size 0.22µm, volume 3ml, provided by MSI). Samples were centrifuged at 900 g for 30 minutes according to TAPPI UM 256. After centrifugation, the moisture content of the samples was determined by weighing immediately and also after drying at 105 °C for 2 hours and cooling in a desiccator jar (anhydrous calcium sulfate) for 30 minutes.

Cellulose Viscosity

In the case of unbleached kraft pulp, a sodium chlorite procedure was applied to measure the cellulose viscosity. Six percent of sodium chlorite solution was prepared according to the following formula: 15 g of sodium chlorite, 5 g of sodium acetate, 10 ml of glacial acetic acid and distilled water that brings the final solution volume to 250 ml. The volume of sodium chlorite solution needed to react with all of pulp lignin is based on the equation (1):

$$V = \frac{40\% * w}{6\%} \quad (1)$$

Where:

V: the volume of 6% sodium chlorite solution, *ml*

w: the weight of pulp sample based on oven-dried, *g*

The necessary amount of distilled water was added to the sample to bring the final pulp solution to 1% consistency. The sample was torn into small pieces, added to part of calculated distilled water, and disintegrated in a blender for one

minute. The remainder of the calculated distilled water was used to transfer all of the pulp from the blender to a flask. After that, the calculated sodium chlorite solution was added to the flask. The retention time for the mixture was 24 hours with occasional swirling of the pulp slurry. After the period of retention, the pulp slurry was thoroughly washed by deionized water and then made into a fiber pad on a filter paper (Whatman #4) in a Büchner funnel with vacuum. The formed pad was placed between two sheets of blotter paper and dried for 24 hours at room temperature. Twenty-five milliliters of distilled water were added to 0.25 g (oven dried basis) air-dried fiber pad in a stomacher bag. After one-minute of beating at high speed, twenty-five milliliters of 1 M cupriethylenediamine (CED) were added to the stomacher bag, followed by another two-minute beating at high speed. 7.2 ml beaten slurry was pipetted into a viscometer tube, which was placed in temperature controlled water bath (25 °C). After five minutes temperature equilibrium, the slurry was drawn by aspirator bulb over top line of the viscometer. The efflux time was obtained when the slurry was drained from the top line to the bottom line. The CED viscosity was calculated based on the following equation:

$$V = C * t * d \quad (2)$$

Where:

V: viscosity of CED at 25 °C, *cP*

C: viscometer calibration constant

t: average efflux time, *s*

d: density of the pulp solution (1.052)

Fiber Flexibility

The procedure for the fiber flexibility test was already described in our previous work [44-45]. Since these articles have not been published yet, the procedure is repeated here.

In the fiber flexibility test a thin, tangentially-orientated fiber network is formed on the wire of a standard sheet machine. Around 5 ml of pulp slurry (1% concentration) was used to make the fiber network. This procedure was tested in the case of blotter paper. The network is then couched onto a #4 Whatman filter paper using a standard sheet technique, corresponding to TAPPI Method T-205. A glass slide having several thin stainless steel wires ($\varnothing=25\ \mu\text{m}$) attached across its surface in the form of a parallel grid is laid onto the filter paper. The filter paper and slide are then pressed against each other between two sets of water-saturated blotters in a regular handsheet press. After a two-minutes pressing at 50 psi, the glass slides are separated from the blotters and filter paper. The fibers adhere to the slide and are viewed in a microscope under incident light. The areas of intimate contact between the fibers and the glass appear dark, and the area that is not in contact, for instance, as the fibers cross over the wire, is less visible. The explanation of the incident light image is based on the theory of thin film interference [46]. It makes sense that the non-contact length is related to the flexibility of the fiber, and as the fiber becomes more flexible, this distance will become reduced. The detailed procedure for preparing slides appears in the literature [37]. Images were captured by a camera attached to a microscope. Image analysis software (Image-Pro Plus 4.0) was used on the digital images to

measure the width and less-visible length of fiber crossing over slide wires. Around 100 fibers were chosen for a standard flexibility testing.

Figure 7-1 shows the setup for the fiber flexibility test. Figure 7-2 shows an enlarged picture of a fiber crossing over wires. Image analysis software (Image-Pro Plus 4.0) was used to capture the pictures and measure the width and the less-visible length (L) of the fibers crossing over slide wires.

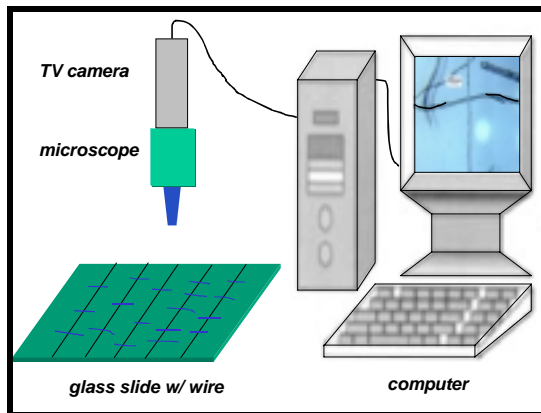


Fig. 7-1. Schematic diagram of flexibility setup

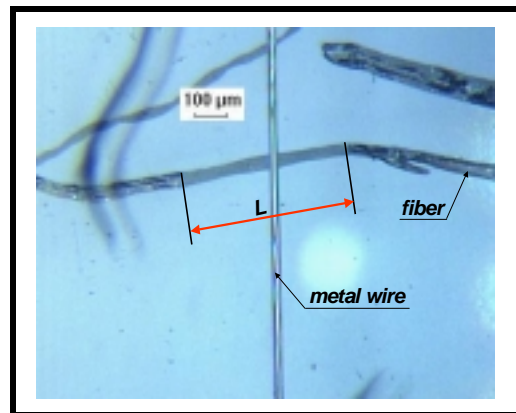


Fig. 7-2. Enlarged picture of a fiber under microscope

The flexibility can be expressed as follows:

$$Fiber\ Flexibility = \frac{1}{EI} = \frac{72d}{PWS^4} \quad (3)$$

Where:

E : modulus of elasticity, $N \cdot m^{-2}$

I : moment of inertia, m^4

d : wire diameter, m

P : pressing pressure, $N \cdot m^{-2}$

W : projected fiber width, m

S : a mathematical estimate of the loaded fiber span, m

According to Cresson [47], equation (4) is a correct form to calculate the loaded fiber span based on the Pythagorean Rule:

$$S = \sqrt{d^2 + \left(\frac{L}{2}\right)^2} \quad (4)$$

Where:

d: wire diameter, *m*

L: less-visible length, *m*

S: a mathematical estimate of the loaded fiber span, *m*

The detailed derivation of equation (3) can be found in a paper of Steadman and Luner [37]. In the present study the geometric mean was used to represent the fiber flexibility of samples instead of the median used by Steadman and Luner [33, 35, 37]. Since the maximum may be 1000 times the minimum in the data, according to Dickey [48] when the data is in such a range, a good approach is to analyze the results using logarithmic plots. He suggested reporting the geometric mean, which is somewhat like the median. Researchers are able to perform statistical modeling on the log scale and test the hypotheses, whereas the distributional results and inference for medians is not so well developed. In this study, a t-test can be used when determining the effect of sugars on fiber flexibility because the distribution of data on the log scale fits a normal distribution.

Effects of Papermaking Process Variables on Fiber Flexibility

Thirty grams of pulp were taken from cold storage and refined with a PFI mill (9000 revolutions). The procedure for refining pulp by PFI followed TAPPI

test T-248. The refined pulp (10% consistency) was put in a zip-lock plastic bag and stored in a cold room for future use.

One gram (based on O.D.) refined pulp was taken from cold storage, soaked in deionized water for 2 hours before being dispersed in a disintegrator for 5 minutes. It was then washed immediately in a large excess of deionized water. After that, different procedures were adopted for specific experiments.

Effect of pH

The washed fiber slurry was divided into 4 portions. Each portion was adjusted to a certain pH value (pH=3, pH=4.5, pH=6 and pH=8) by addition of 4N H₂SO₄ or 0.25N NaOH. The adjusted fiber slurry was stored in this condition for 12 hours before the fiber flexibility was tested.

Effect of Salt Concentration

The washed fiber slurry was divided into 4 portions. Each portion was adjusted to certain conductivities (500 μS/cm, 1000 μS/cm, 2000 μS/cm and 5000 μS/cm) by Na₂SO₄ solution (2% concentration). The adjusted fiber slurry was stored in this condition for 12 hours before the fiber flexibility was tested.

Effect of Hardness

The washed fiber slurry was divided into 3 portions. Each portion was adjusted to certain hardness (100 ppm, 200 ppm, 400 ppm) by addition of CaCl₂ solution (1% concentration). The adjusted fiber slurry was stored for 12 hours before the fiber flexibility was tested.

RESULTS AND DISCUSSION

Effects of pH on Paper Strength

Figure 7-3 shows the effect of sheet-forming pH on the tensile strength of handsheets. The limit bars represent 95% confidence intervals for the means of physical test results. Figure 7-3 shows a distinct difference in breaking length when comparing the virgin sheets to the recycled sheets. However, within the precision of the tests, no pH effect was observed in either case. The lack of pH effect in Fig. 7-3 was surprising in light of previous work reported by Lindström and Carlsson [1]. Possible differences in materials that might explain the different results include (a) in the cited work the pulp was intensively washed, so that pulp might not have realistic levels of multivalent ions in it, and (b) it is possible that the pulp used in the present work has a lower level of carboxyl groups. However, further work, following the procedure described by Wilson [49], showed that the content of carboxyl groups of this pulp was 16.58 meq/100g. The result was the average of two replicate measurements. This amount of carboxyl groups is close to that which was reported for unbleached pulp with 55.5% yield in the work of Lindström and Carlsson [1]. Therefore, by process of elimination, it seems more likely that the reason for the lack of pH response is the existence of multivalent metal ions in the pulp of the present study.

It is noted that our pulp was screened and washed by tap water, where calcium ions and magnesium ions are rich. According to the work of Scallan and Grignon [17], the effect of a range of different cations on increasing paper

strength followed the order $M^{+++} < H^+ < M^{++} < M^+$. He also concluded that the composition of water supply could affect the paper properties and fibers would preferentially pick up the higher valency ions. In his study, pulps were converted to hydrogen forms and then thoroughly washed by deionized water before converted to other ionic forms. All traces of metal ions except the targeted ions had been removed prior to sheet forming. In this present study it is predicted that adding sodium hydroxide to adjust pH of pulp had less effect on paper strength since it is presumed that pulp slurry was saturated with calcium ion or magnesium ion. According to Ackermann *et al.*, the most common cations are hydrogen, calcium, and aluminum in conventional papermaking [29].

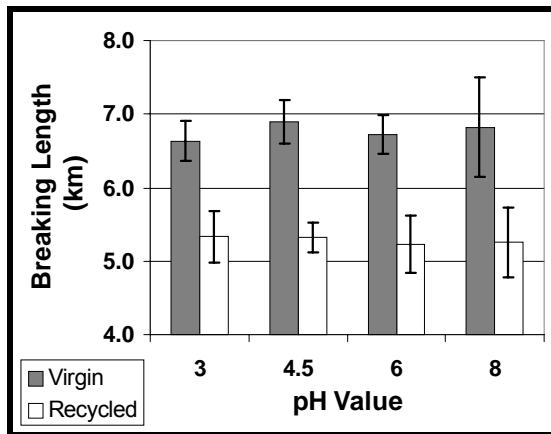


Fig. 7-3. Effect of sheet forming pH on the tensile strength of paper

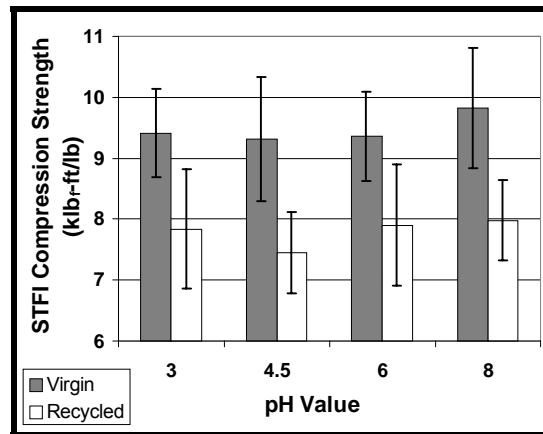


Fig. 7-4. Effect of sheet forming pH on the compression strength of paper

Unbleached kraft pulp is a major component of furnish for linerboard. One of the major end-uses of linerboard is to produce a carton or corrugated box to protect the contents against compression forces during packing, storage and distribution. In some paper grades the most important property of paper strength is tensile strength. However, corrugated containers seldom fail in a tensile mode. Rather, compression strength of the linerboard is a much better predictor of

failure. With stack heights constantly increasing in modern warehouses and on pallets, the compression strength of corrugated boxes, always a matter of concern, is becoming more important to converters and end users.

Figure 7-4 shows corresponding results in the case of STFI compression strength. Still no significant effect of pH on STFI compression strength was found. This result provided further evidence to show that sheet forming pH had less effect on the strength of paper made from multivalent metal ions-rich pulp. It was also found that the paper strength of recycled papers showed no significant difference. This is in line with our previous work [50], which showed that the relative change of breaking length during recycling is almost proportional to the relative change of compression strength due to recycling. It is worth noting that tensile strength data tend to be more repeatable than compression strength data.

Effect of pH on WRV

WRV is an index for the degree of fiber swelling. Figure 7-5 shows water retention values (WRV) for the same pulp samples. These data were obtained for pulp samples before forming and drying of the corresponding set of paper. The decreases in WRV with drying and re-slurrying of the pulp are consistent with the strength results. Again there was no significant effect of pH on water retention value, an observation that is consistent with the paper strength results. It is reasonable to conclude that the metal ions dominated fiber swelling, since pulping and washing processes result in many cations in the fibers. Our previous work [51] also demonstrated that there was no significant effect of initial pH on

water retention value of unbeaten kraft pine pulp after they are later re-dispersed in water at neutral pH.

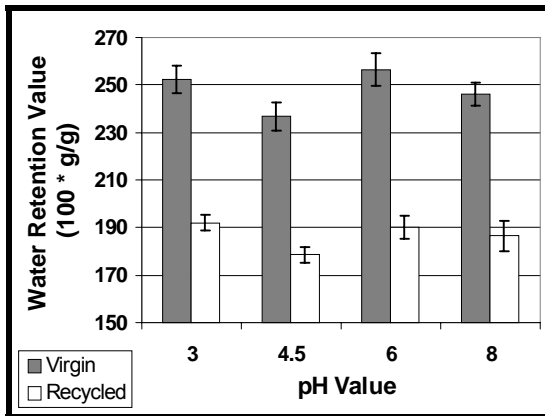


Fig. 7-5. Effect of sheet forming pH on the water retention value of unbleached kraft pulp

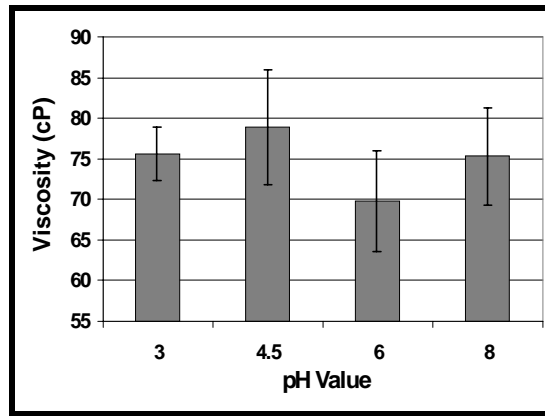


Fig. 7-6. Effect of sheet forming pH on the degree of polymerization of cellulose in the unbleached kraft pulp

Effect of pH on the Cellulose Viscosity

Although one cannot conclude paper strength properties from the molecular mass of cellulose in a sample of fibers, it is reasonable to expect that the breakdown of cellulose molecular structure will affect their performance. In this study unbeaten unbleached kraft pulp was taken from a cold room and dispersed in a TAPPI disintegrator for 5 minutes. The dispersed slurry was separated to four portions. Each portion was adjusted to a certain pH value (pH=3, pH=4.5, pH=6 and pH=8) with either H₂SO₄ or NaOH. The adjusted slurry was stirred for 10 minutes before making handsheets with matched pH-adjusted water. The handsheets were dried in an oven for 40 minutes at 150 °C before viscosity test.

As shown in Fig. 7-6, there was no significant effect of the pH conditions before drying on the viscosity test results. The practical significance of the results in Fig. 7-6 is to suggest that even at pH=3 there was no substantial

acceleration of the proposed hydrolysis reaction, and that ordinary papermaking practices are not expected to drastically reduce cellulose molecular mass, throughout the common pH range of papermaking.

Effect of pH on Fiber Flexibility

Over the past two decades it has been common for paper mills to change their aqueous conditions of papermaking from acidic to alkaline. Part of the reason for this shift has been a belief that paper made under alkaline conditions is stronger than paper made under acidic conditions, all other things being equal. It has been said that fibers swell and become more flexible under alkaline conditions [52]. However, no data have been available to prove the effect of pH on the fiber flexibility. In our study, the fiber flexibility test was conducted at different pH conditions. Figure 7-7 shows that the flexibility of refined fiber was higher under alkaline conditions than that under acidic conditions. A T-test showed that the effect was significant at a 95% confidence level. Thus the fiber flexibility test provided direct evidence to support the claim [52].

It is noted that there was not a significant effect on fiber flexibility at different acidic pH values. It is puzzling why papers made under alkaline conditions did not show higher strength, since these papers were made from fibers having higher flexibility. There are two possible reasons. One possible explanation is related to experimental procedure. As described earlier, the fibers involved in the flexibility test in this study were washed by excess deionized water and then soaked 12 hours under targeted pH values before testing, but not converted to hydrogen form as Lindström *et al* did [1-3, 17, 39]. It appears likely that the fibers

related to fiber flexibility test had a behavior that is intermediate between the extreme represented by cited articles [1-3, 17, 39] and fibers involved in paper strength measurement. Another possible reason is that there was an effect of pH on strength, but that the effect was small relative to the reproducibility of the experimental results.

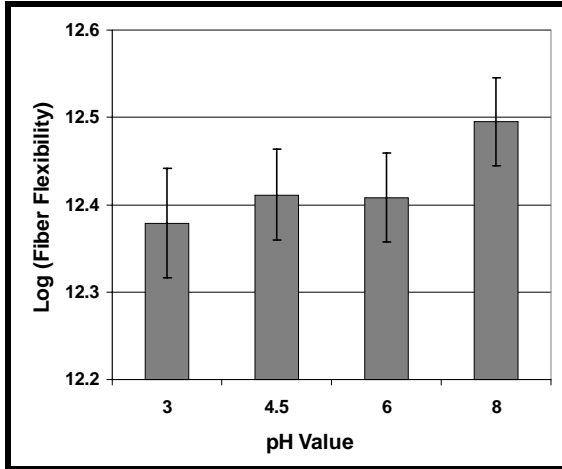


Fig. 7-7. Effect of pH on the flexibility of virgin refined unbleached kraft fibers

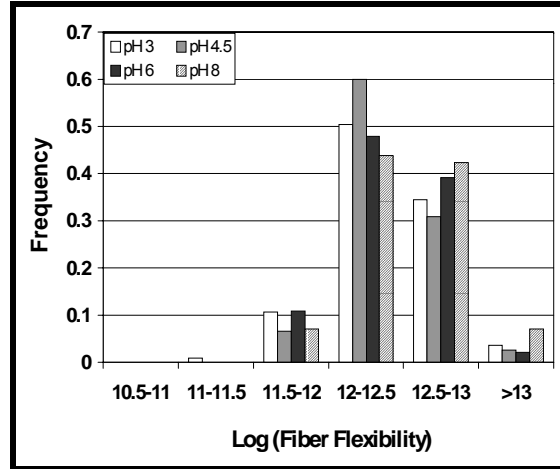


Fig. 7-8. Effect of pH on the flexibility distribution of virgin refined unbleached kraft fibers

Figure 7-8 shows the distributions of fiber flexibility found in this study. It can be observed for all samples that there was an approximately normal distribution of fiber flexibility when plotted on a logarithmic scale [48]. It is clear that fibers under alkaline condition fall within the range of higher flexibility compared to the fibers under acidic conditions.

In order to confirm whether fibers become flexible under alkaline conditions and eliminate the influence of refining, the effect of pH on the flexibility of the same type fibers but without refining was also observed. In this case, the condition of pH=10 was also considered. As shown in Fig. 7-9, virgin unrefined

fibers had higher flexibility under alkaline condition and even at a neutral condition.

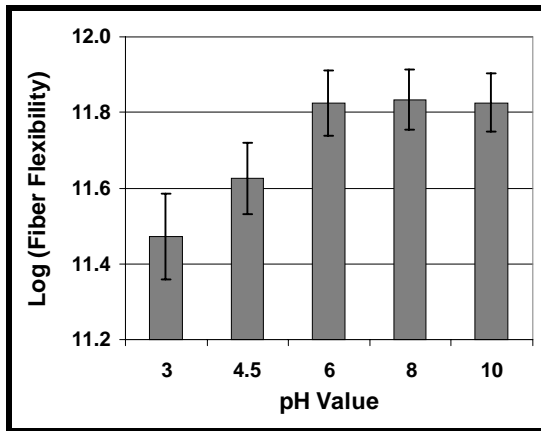


Fig. 7-9. Effect of pH on the flexibility of virgin unrefined unbleached kraft fibers

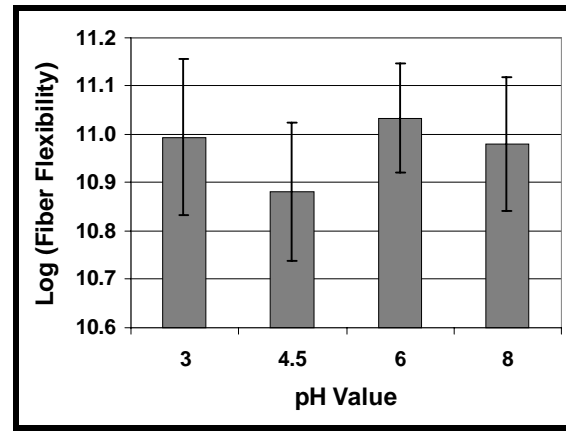


Fig. 7-10. Effect of pH on the flexibility of oven-dried unrefined unbleached kraft fibers

As described earlier, according to Klungness [12], the addition of sodium hydroxide to waste paper during recycling restored the bonding potential either by removing the contaminants from fiber surface or by chemically restoring the bonding potential of fibers. In our study, the recycled fibers are clean, without any of the non-fibrous contaminants usually associated with recycling. It is of interest to know whether the rewetting pH affects the flexibility of recycled fiber. The results maybe provide a hint to determine which factor dominates the recovery of fiber bonding potential [12]. At this point, virgin unrefined fibers were dried in an oven at 105 °C for 12 hours, and soaked in deionized water 12 hours before being dispersed in a TAPPI disintegrator for 5 minutes. This was followed by the procedure for the effect of pH on refined fibers, as described in the experimental section. Figure 7-10 shows that rewetting pH had no significant effect on fiber flexibility.

Effect of Salt Concentration on Fiber Flexibility

When mills close up their white water systems, the level of dissolved substances increases. Conductivity is a property that papermakers can measure to get an indication of trends in the levels of ionic materials in water. A typical conductivity of process water may be as low as 500 $\mu\text{S}/\text{cm}$ in a clean, bleached kraft paper machine system that uses of 10,000 gallons or more of fresh water to produce each ton of pulp. Conductivities in the range of 1000 to 3000 $\mu\text{S}/\text{cm}$ are common in paper mill system where there is extensive reuse of process water for showers. In certain mills the conductivity is up to 5000 to 20,000 $\mu\text{S}/\text{cm}$, where old corrugated container pulp is being recycled without any discharge of liquid effluent [53].

It is known that the salt concentration of a pulp slurry affects fiber swelling and paper strength [1, 17, 24]. It is of interest to know how the salt concentration affects fiber flexibility. However, data about correlation between fiber flexibility and salt concentration from publications is scarce. In this study, four levels of conductivity were selected to carry out the experiment: 500 $\mu\text{S}/\text{cm}$, 1000 $\mu\text{S}/\text{cm}$, 2000 $\mu\text{S}/\text{cm}$ and 5000 $\mu\text{S}/\text{cm}$. As expected, fiber flexibility was reduced with increasing salt concentration of the pulp slurry as shown in Fig. 7-11, according to results of fiber swelling and paper strength. As described earlier, WRV of fibers decrease with increasing salt concentration [1, 23] due to the shielding effect [1], which reduces the repulsion force between the charged groups on the fiber surface, or due to reduced osmotic pressure difference [24].

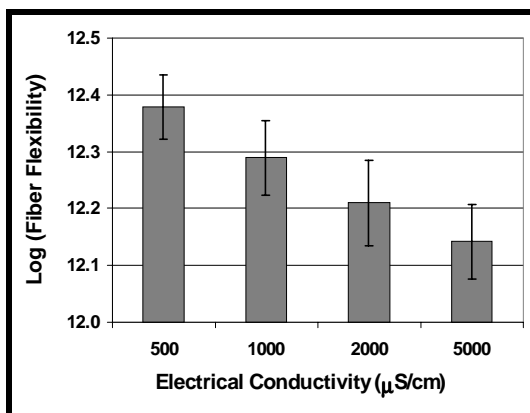


Fig. 7-11. Effect of salt concentration on the flexibility of virgin refined unbleached kraft fibers

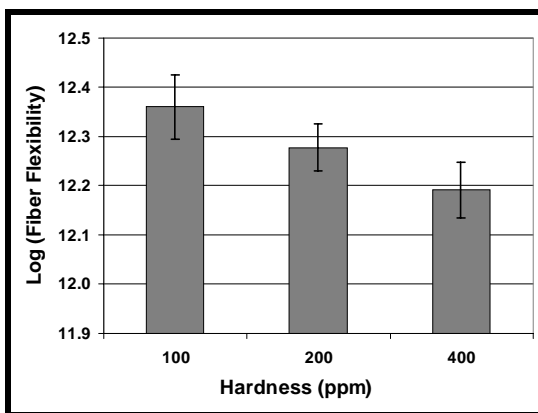


Fig. 7-12. Effect of hardness on the flexibility of virgin refined unbleached kraft fibers

Effect of Water Hardness on Fiber Flexibility

The technical definition of water hardness is the concentration of dissolved divalent calcium and magnesium cations in water, independent of anions present, expressed as ppm calcium carbonate [54]. Because relatively hard water is used in many paper mills and hardness is an important index for water quality, it is important to know the effect of hardness on the fiber properties. At the same time it is well known that calcium ion forms a complex with carboxyl group. It is also known that the calcium ion has more effect on water retention value than the sodium ion [17]. Therefore, it was of interest to know the effect of water hardness on the fiber flexibility. Typical hardness of soft water is in the range of 0-75 ppm, moderately hard water with the range of 75-150 ppm, hard water within the range of 150-300 ppm, and very hard water over 300 ppm [55]. In this present study, three levels of hardness (100 ppm, 200 ppm and 400 ppm) were chosen to determine the effect of hardness on fiber flexibility. Figure 7-12 shows that the fiber flexibility was reduced with increasing hardness of pulp

slurry. This result is as expected, because increased water hardness means increased cations concentration, which in turn reduces fiber swelling. It is evident that the cations contribute to the effect. The conductivity measurements on the three levels of hardness showed that 397 $\mu\text{S}/\text{cm}$, 740 $\mu\text{S}/\text{cm}$ and 1368 $\mu\text{S}/\text{cm}$ represented 100-ppm, 200-ppm and 400-ppm pulp slurries respectively, with respect to CaCl_2 addition. It is noted that the conductivity of tap water in our lab was 390 $\mu\text{S}/\text{cm}$, and pulp slurry before hardness adjustment was 3.9 $\mu\text{S}/\text{cm}$. If one compares Fig. 7-11 with Fig. 7-12, it was found that fibers showed lower flexibility when using calcium chloride to reach the same targeted conductivity of fiber slurries, compared to fibers in the presence of at the same conductivity in the presence of sodium sulfate. The present results provided indirect evidence to support the conclusions that calcium ion had greater effects on fiber swelling and paper strength, compared to the sodium ion [17].

CONCLUSIONS

Recycled handsheets had lower paper strength compared with virgin handsheets at all pH values considered during paper formation within the range of pH 3 to pH 8. There was no significant effect of pH on paper strength within this range. The lack of effect of sheet forming pH on paper strength implies that under practical papermaking conditions, adjusting sheet forming pH may not be an effective tool for increasing paper strength in the case of unbleached kraft pulp of the type used in the present work. The results from water retention value and cellulose viscosity measurements also supported this conclusion.

The fiber flexibility tests showed that the method is useful to determine the flexibility of individual fibers. Fibers were more flexible under alkaline conditions than those under acidic conditions. Fibers became less flexible with increasing salt concentration and hardness.

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CHAPTER 8

Changes to Unbleached Kraft Fibers Due to Drying*

ABSTRACT

Drying of unbleached kraft pulp in the laboratory revealed two main stages in its response to increasing temperature of drying. The first stage was characterized by significant decreases in water retention value, capacity to adsorb a cationic polymer, dry strength, and apparent density of handsheets formed after re-slurrying the pulp with no additional treatment. These changes, which were independent of the drying temperature, were attributed to the action of capillary forces in the closure of micro-pores in the cell wall during the initial drying. The second stage was characterized by further significant decreases in all of the same parameters when drying temperatures became as high as 150 °C or higher. In addition, high-temperature drying also resulted in a loss of molecular mass of the cellulose, as revealed by viscosity tests. The results suggest that whereas some irreversible changes in fiber properties are unavoidable during conventional papermaking practices, further losses in the bonding ability of unbleached kraft fibers can be caused by over-drying.

INTRODUCTION

Unbleached softwood kraft fiber is among the most widely used natural materials for packaging, most notably in linerboard for corrugated boxes. In 2001 the world production rate of containerboard was about 90 billion tons [1], which

* This chapter has been modified from the following publication: *Progress in Paper Recycling*, 12(3): 11-20, 2003.

was about 28% of the total world production of all paper products. Unbleached kraft pulp is the main component of most of this production. Another remarkable statistic is the recycling rate; approximately 70% of the fiber content of corrugated containers made in the U.S. currently becomes recycled, primarily for the production of recycled linerboard and corrugating medium [2, 3].

The goal of the present work is to quantify some factors causing the properties of recycled unbleached softwood kraft pulp fibers to differ from those of the never-dried unbleached kraft pulp (UBK). This type of fiber is a major component of old corrugated container (OCC). OCC also can contain hardwood kraft and neutral sulfite semichemical fibers and various recycled fibers.

Many previous studies have demonstrated a significant loss of paper strength when one compares recycled kraft fibers to never-dried kraft or sulfite fibers under matched conditions of paper forming [4-18]. In industrial practice some of the difference between OCC and UBK can be attributed to contamination. For example, the OCC may contain mineral fillers from white-top grades, and these fillers will tend to decrease bonding strength between the fibers. Also, the relatively long softwood fibers in conventional linerboard stock become "diluted" by the shorter, high-yield hardwood kraft fibers, which are often the main component of primary corrugated medium. However, it also has been shown that a significant contribution to the loss of bonding strength between fibers in recycled linerboard is due to the drying of the fibers during the initial and possible later cycles production [5, 7, 10, 14-15, 17-18].

Conditions of drying also can affect the degree of polymerization of bleached kraft fibers [19-21]. Since typical unbleached kraft fibers start with a higher degree of polymerization, compared to typical bleached kraft fibers, it is of interest to know whether they are susceptible to the same kind of changes under conditions corresponding to the drying of paperboard. Though it is not known to what extent the molecular mass of cellulose relates to paper strength properties, it was found that the degradation of cellulose caused the loss of fiber strength [22]. It is reasonable to expect that breakdown of the molecular structure of the fibers to impact their performance, either in terms of paper recycling or a source of feedstock for bleached kraft pulp manufacture [23].

Previous investigators have proposed a series of physical changes that may occur when kraft fibers are dried by heating [11, 17, 24]. Partly irreversible closure of pore spaces within the cell wall of fibers appears to take place relatively early in the drying process, as the paper is dried from about 45 or 50% solids (after pressing) to about 60% solids [4, 11, 24-26]. Results of solute-exclusion tests have been interpreted as showing that the pore spaces involved in the irreversible closing process are of intermediate size, possibly in the range of 5-20 nm [4, 27]. Recently it has been suggested that such estimates of pore size need to be revised upwards due to a neglect of consideration of osmotic pressure effects and excluded volume effects in the original studies [28]. It also has been proposed that further shrinkage of fibers, not associated with observable pores, occurs nearer to the end of the drying process as the last remaining water (bound water) is evaporated [24].

Some key properties to consider when characterizing pulp slurries with respect to their ability to form inter-fiber bonds are their fiber length, degree of swelling in water, effective surface area in the wet state, and their flexibility. A recent report showed significant changes in fiber flexibility upon drying a sample of the same unbleached softwood kraft pulp considered in the present work [29]. The wet flexibility of never-dried fibers was found to depend on such factors as water hardness, ionic strength (sodium sulfate), and pH. Drying and rewetting of those fibers to approximately 5% moisture at 105 °C, followed by redispersal in water, resulted in a significant loss of wet flexibility.

The water retention value (WRV) test has been widely used to estimate the water content of the cell walls of fibers [30-32]. A wet mat of fibers is placed upon a porous glass disc within a centrifuge tube and then accelerated under standard conditions such as 900 g [30] or 3000 g [33-35]. Though this method provides no detail regarding the size or size distribution of pores in the fibers, the tests are relatively simple and quick. One of the main uncertainties in interpretation of WRV results is the possible contribution of a film of water associated with the external surfaces of the fibers [34-35], a contribution which may depend on the amounts of pulp used in replicate tests [36]. It has been proposed that polyelectrolytes retained in the paper also can influence the amount of surface water on the fibers [34, 37]. These uncertainties were minimized in the present study, which involved a relatively low level of refining, a relatively low fines content, and no polymeric additives.

As shown by some previous work [38-39], relative differences in the externally accessible surface area per unit mass of fiber can be evaluated by means of polyelectrolyte titrations. To run this type of analysis one adds a known excess of cationic polyelectrolyte to the pulp, mixes it well for a defined time period, separates the solid phase from the filtrate, and then evaluates the filtrate for residual cationic polymer. Some prerequisites to be able to apply this type of test effectively include (a) the pulp must have been sufficiently washed to remove most of the colloidal material, (b) the salt content should be relatively low, and (c) the polyelectrolyte should be chosen to be in a suitable size range having a mean value relatively near to the size of typical pore spaces in the fibers. Recent work of this nature showed that drying and redispersing of kraft fibers can significantly reduce their accessibility to polyelectrolytes [38].

EXPERIMENTAL

Materials

Pulp: Never-dried, unbleached kraft (UBK) pine pulp was obtained from the Mansfield, Louisiana mill of International Paper. The pulp was screened, centrifuged to around 30% consistency and fluffed before being stored in a cold room until use. The initial value of Canadian Standard Freeness [40] before making handsheets was 739 ml a low degree of refining. This value is higher than typical during production of linerboard from virgin kraft pulp, although it is a practice in some linerboard operations to maintain as high freeness as practical to maximize compression strength and dewatering rates. In addition, loss of some fines during screening is expected to have increased the freeness value.

Chemicals: Poly-diallyldimethylammonium chloride (poly-DADMAC) used to test the polymer adsorption capacity of pulp fibers, was Alcofix® 169 from Ciba Specialty Chemicals. The anionic titrant was 0.001 N poly-(vinylsulfate potassium salt) solution (PVSK), brand S5432 from Ondeo Nalco. Polymers were used without further purification.

Equipment: A Seward laboratory blender (Stomacher 80, Brinkmann) and Constant Temperature Bath (Model M-1, Cannon Instrument Company) were used to measure cellulose viscosity. An Electrokinetic Charge Analyzer (ECA 2000P, Chemtrac System Inc.) was used to measure streaming current, assisted with a Müteck PCD Titrator to improve the precision of results.

Procedures

Effect of Drying Temperature on Paper Strength

In this study, the basis weight of handsheets was 120 g/m², instead of 60 g/m² as specified in the TAPPI Method T-205, due to the requirements of the STFI compression strength test [41]. Figure 8-1 shows the procedure used to study the effect of drying temperature of primary handsheets on the paper strength of secondary handsheets. Handsheets were dried following TAPPI Method T402, with the following modifications. Except for the air-drying condition (25 °C) under which primary handsheets were dried in a TAPPI conditioned room for twelve hours, the other drying conditions involved an air-convection oven. Each ten primary handsheets were dried in the oven for fifteen minutes at different targeted temperatures (90 °C, 105 °C, 120 °C, 150 °C and 175 °C)

respectively before being moved to a TAPPI conditioned room to equilibrate over night.

Dried handsheets were soaked in water for at least four hours before being dispersed in a TAPPI disintegrator for five minutes. Freeness, water retention value and fiber surface charge were measured before making secondary handsheets. In the case of secondary handsheets, all handsheets were dried in a TAPPI conditioned room overnight before the measurement of paper physical properties.

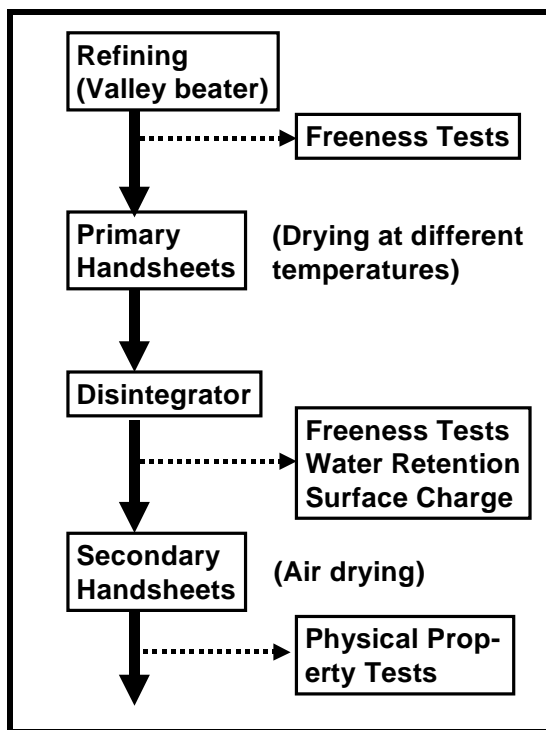


Fig. 8-1. The procedure for the effect of drying temperature of primary handsheets on the physical properties of recycled handsheets

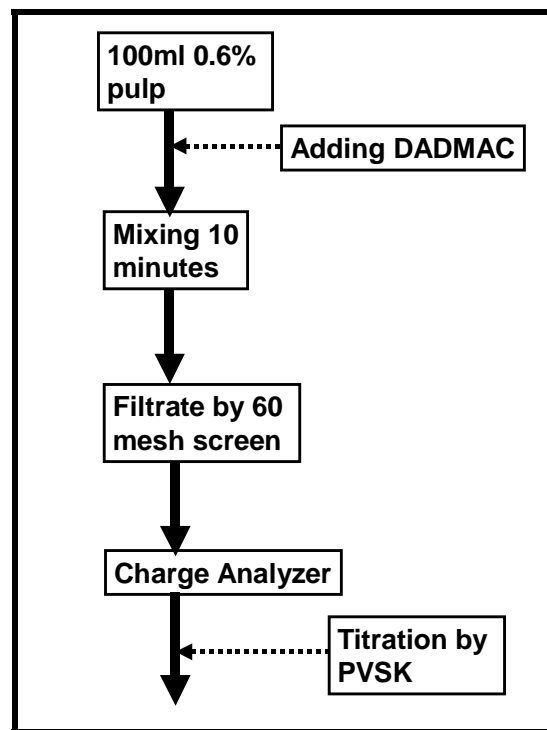


Fig. 8-2. The procedure for determining the amount of poly-DADMAC adsorption on fiber surface

Water Retention Value

Water retention value tests (WRV) were conducted according to TAPPI Useful Method 256 [30], with some modifications. Prior to measurement, the

pulp samples were disintegrated for 5 minutes (15,000 revolutions, TAPPI Method 205), thoroughly washed in a large excess of deionized water, and allowed to stand in water over night. Although loss of fines can be expected, the effects were expected to be small in the present work with UBK pulp due to the fact that the refining level was low, and the pulp previously had been washed. Following further washing, the pulp was collected on a vacuum filter and dewatered to 25% solids. Moist samples of pulp, equivalent to 0.16 g dry mass, were placed in sintered centrifuge tubes (pore size 0.22 μm , volume 3 ml, provided by MSI). Samples were centrifuged at 900 g for 30 minutes. After centrifuging, the moisture content was determined by immediate weighing, and also after drying at 105 °C for 2 hours and cooling in a desiccator jar for 30 minutes.

Adsorption of Poly-DADMAC

A streaming current procedure was used to determine the poly-DADMAC adsorption on fiber surface. As shown in Fig. 8-2, an excess amount of 0.4% by mass poly-DADMAC was added in 100 ml aliquots of 0.6% consistency pulp with stirring over few seconds. The mixture was stirred for 10 minutes before being passed through a 60-mesh stainless steel screen. The filtrate was evaluated with an Electrokinetic Charge Analyzer (ECA 2000P), using PVSK solution to titrate the filtrate charge back to zero. The fiber saturation with poly-DADMAC was determined by the amount of poly-DADMAC that was necessary to add to the pulp slurry to neutralize the fiber surface charge.

Effect of Drying Temperature on Pulp Viscosity

The procedure related to the effects of drying conditions on the viscosity test is a little different with that which was used for experiments related to paper strength. First, only one handsheet was made for each drying condition. Second, the handsheet was only passed through first cycle of pressing before being dried. Third, the dried handsheets were placed in plastic zip-loc bags until the measurement of viscosity, after the oven-dried handsheets were equilibrated over night in a TAPPI conditioned room. Parallel experiments showed that the final moisture contents of the paper samples, at the end of the drying cycle, were as follows: 9.32% after 12 hours of air-drying under TAPPI conditions; 2.11% after 15 minutes oven drying at 90 °C, 2.07% after 15 minutes at 105 °C, and essentially zero after fifteen minutes of oven drying at 120 °C or above. The condition of zero moisture was calibrated relative to a two-hour drying treatment at 105 °C.

To add perspective regarding the drying conditions specified above, it should be noted that final moistures below about 5% represent cases of significant “over-drying”. For this reason the temperature conditions of 90 degrees and higher used in the present work may result in greater than typical losses in fiber bonding ability. Linerboard is more typically dried to 7 to 9% moisture at the reel of the paper machine. In a future study it would be worth considering the more experimentally challenging aim of using different temperature conditions to dry the fibers to a selected final moisture content. Another issue for future consideration is whether rapid drying will cause

significant surface hardening of fibers before the interior of the same fiber have become dry, possibly affecting the overall results.

Different procedures were used for evaluation of the molecular mass of cellulose in the bleached and the unbleached kraft pulps [42]. In both cases the consistency of the sample was measured to determine the amount of wet pulp corresponding to 0.25 g, oven-dry basis. In the case of unbleached kraft pulp, sodium chlorite procedure was applied to measure the cellulose viscosity. Six percent of sodium chlorite solution was prepared as following formula: 15 g of sodium chlorite, 5 g of sodium acetate, 10 ml of glacial acetic acid, and distilled water that brings the final solution volume to 250 ml. The volume of sodium chlorite solution needed to react with all of pulp lignin (the Kappa number [43] of pulp in this study is 97) is based on the following equation (1):

$$V = \frac{40\% * w}{6\%} \quad (1)$$

where:

V: the volume of 6% sodium chlorite solution, *ml*

w: the weight of pulp sample based on oven-dried, *g*

The necessary amount of distilled water that was added to the sample is to bring the final pulp solution to 1% consistency. The sample was torn into small pieces, added part of calculated distilled water, and disintegrated in a blender for one minutes. The remainder of the calculated distilled water was used to transfer all the pulp from the blender to a flask. After that, the calculated sodium chlorite solution was added to the flask. The retention time for the mixture was 24 hours with occasional swirling of the pulp slurry. After the retention, the pulp slurry was

thoroughly washed by deionized water and then made into a fiber pad on a filter paper (Whatman #4) in a Büchner funnel with vacuum. The formed pad was placed between two sheets of blotter paper and dried for 24 hours at room temperature. Twenty-five ml of distilled water was added to 0.25 g (oven-dried basis) air-dried fiber pad in a stomacher bag. After one-minute beating at high speed, twenty-five ml of 1 M cupriethylenediamine (CED) was added to the stomacher bag, followed by another two-minute beating at high speed. 7.2 ml beaten slurry was pipetted into a viscometer tube, which was placed in temperature-controlled water bath (25 °C). After five minutes temperature equilibrium, the slurry was drawn by aspirator bulb over the top line of the viscometer. The efflux time was obtained when the slurry was drained from the top line to the bottom line. The CED viscosity was calculated based on the equation (2):

$$V = C * t * d \quad (2)$$

Where:

V: viscosity of CED at 25 °C, *cP*

C: viscometer calibration constant

t: average efflux time, *s*

d: density of the pulp solution (1.052)

RESULTS AND DISCUSSION

Effect of Drying Temperature on Paper Strength

Results of the paper strength tests are shown in Figs. 8-3 and 8-4. Tensile and compression strength values are shown as a function of previous drying

history of the fibers. Limit bars indicate 95% confidence intervals of the mean. The “control” data in both figures correspond to paper handsheets formed from the never-dried pulp. The data can be summarized in terms of (a) an initial drop in strength properties due to the drying process, regardless of temperature, (b) a range of temperatures up to about 150 °C in which the strength did not decrease much beyond the range of statistical significance, if at all, and (c) a further marked decrease in strength due to exposure to drying temperatures above about 150-175 °C.

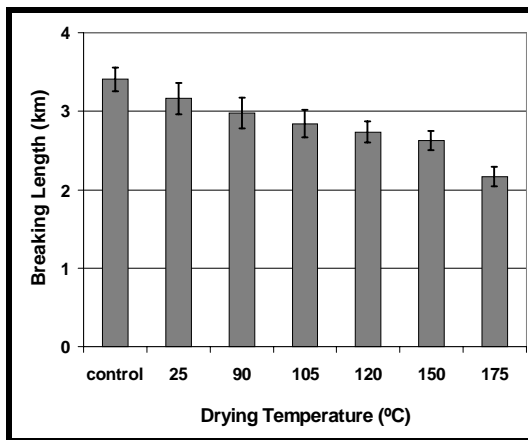


Fig. 8-3. Effect of drying temperature of primary handsheets on the tensile strength of recycled handsheets

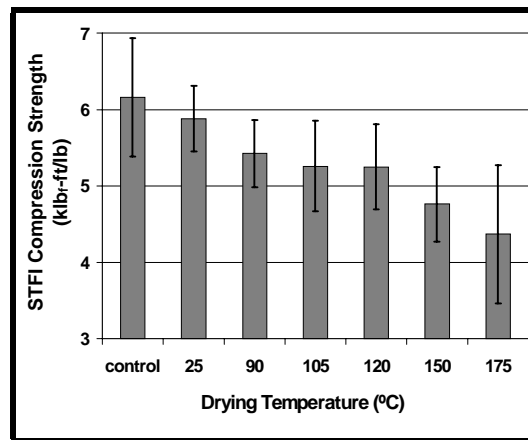


Fig. 8-4. Effect of drying temperature of primary handsheets on the compression strength of recycled handsheets

Apparent density of handsheets sometimes can be used as an indication of fiber flexibility and conformability, if, as in the present case, all of the sheets were subjected to the same conditions of pressing. As shown in Fig. 8-5, the apparent density of handsheets follows the similar trend of strength properties shown in Figs. 8-3 and 8-4. Also previous drying at 150 °C or 175 °C resulted in significant reduction in apparent density values of the recycled handsheets.

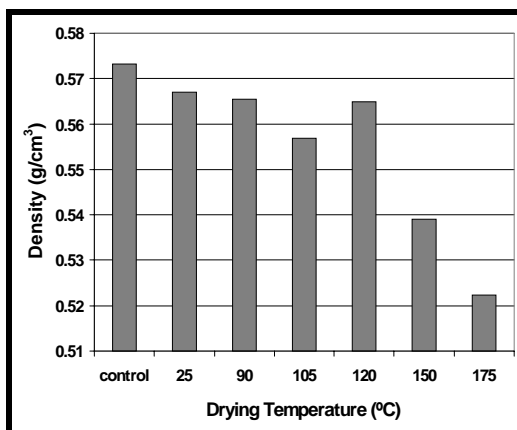


Fig. 8-5. Effect of drying temperature of primary handsheets on the apparent density of recycled handsheets

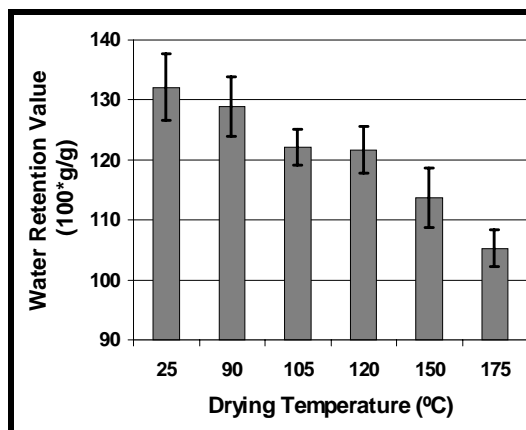


Fig. 8-6. Effect of drying temperature on the water retention value of unbleached kraft fibers

Although no individual fiber flexibility test was conducted in this study, our previous work [29] showed that never-dried fibers had higher flexibility than air-dried fibers, and air-dried fibers had higher flexibility than oven-dried fibers.

Effect of Drying Temperature on Water Retention Value

As shown in Fig. 8-6, the water retention value (WRV) of unbleached kraft pulps was reduced with increasing temperature of drying. The figure appears to show two main steps, during drying at different temperatures. The first step entails a very significant drop in WRV due to drying itself, regardless of the temperature during drying. The WRV of never-dried unbleached kraft pulp was not measured in this series; however, a value within 190% to 220% is expected based on other similar batches of pulp [44]. There was relatively little change in WRV with increasing temperature of drying in the range between about 25 °C and about 90 °C. The second step is represented by a further decline in WRV with increasing temperature of drying above 105 °C.

Freeness testing was used to evaluate the drainage characteristics of pulp slurries. Results showed that recycled pulp had similar freeness values, within the range of 710 ml to 734 ml, due to the drying process, independent of drying temperatures.

Effect of Drying Temperature on Poly-DADMAC Adsorption

Figure 8-7 shows how the temperature of drying affected the amount of the highly cationic, linear polymer, poly-diallyldimethylammonium chloride (poly-DADMAC), remaining on the unbleached kraft after exposure to a known excess, followed by filtration. The two symbols represent two replicate experiments. Again, the largest difference was observed when comparing the never-dried fibers to once-dried fibers, regardless of the temperature of drying. Between 25 °C and 150 °C there was no significant dependency of polymer adsorption on drying temperature. At the highest temperature, 175 °C, there was a further drop in polymer adsorption.

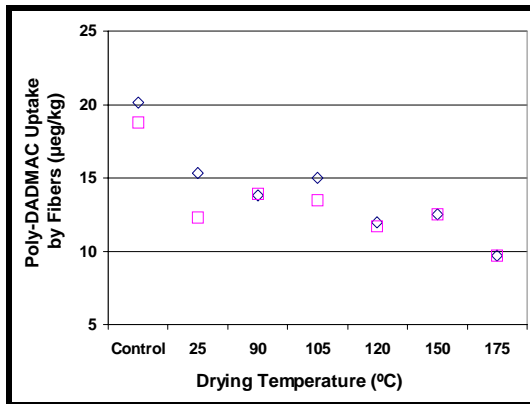


Fig. 8-7. Effect of drying temperature on the amount of poly-DADMAC adsorbed by unbleached kraft fibers

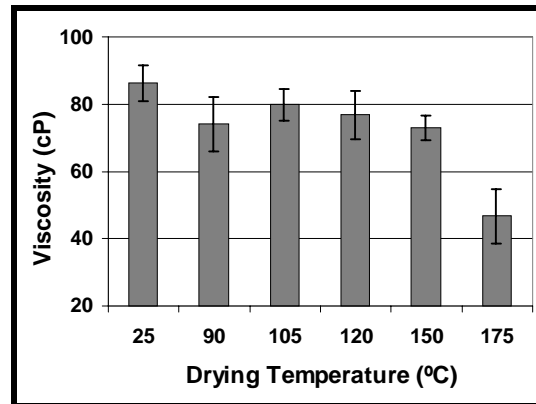


Fig. 8-8. Effect of drying temperature on the amount of poly-DADMAC adsorbed by unbleached kraft fibers

As in work reported by Gruber *et al.* [38] the observed changes in polymer adsorption are consistent with a reduction in surface area that is accessible to the poly-DADMAC molecules. Such a reduction is expected if the process of drying results in closure or significant, irreversible narrowing of pores in the cell walls of the fibers [4]. Based on a nominal molecular mass of approximately 100,000 g/mole of the poly-DADMAC, the critical diameter of pores allowing passage of an average poly-DADMAC molecule is expected to be at least about 5 nm [45]. The reason that this estimate is considered to be a minimum is that it does not take into account the expected expansion of molecular conformation in the case of a charged polymer. Also, a more detailed analysis would take account of osmotic effects [28]. Another potential contributing factor to keep in mind for future studies is the possibility that results may have been affected by changes in the accessibility of fiber lumens due to drying-induced changes in pit borders. The suspected surface-hardening effects mentioned earlier also would be expected to affect the accessibility of the fiber cell wall to penetration by polymers.

Effect of Drying Temperature on Cellulose Mass

As shown in Fig. 8-8, a significant loss in viscosity was apparent after drying unbleached kraft pulp at 175 °C. The limit bars show 95% confidence intervals for the mean. Fifteen minutes of drying treatment at 175 °C resulted in almost a 50% drop. Based on the Mark-Houwink equation [46], $[\eta] = 0.98 \times 10^{-2} DP^{0.9}$, this drop corresponds to a loss of cellulose degree of polymerization (DP) from 24,000 to 13,000.

It is worth noting that the viscosity determination in the case of the unbleached kraft pulps required treatment with sodium chlorite. Since the oxidizing conditions have the potential to cleave cellulose chains, one cannot rule out the possibility that the true values for cellulose DP of the unbleached kraft pulps may have been larger than what is indicated in the figure [42].

Based on the results of a related study [21], the mechanism of cellulose viscosity loss can be understood as random hydrolytic chain scission. The extent of molecular breakdown of the cellulose depends on temperature, aqueous conditions, and the time during which the sample remains wetted during the heat treatment. A key finding of the previous cited work [21] was that heating of bleached kraft fibers in the wet state (in a pressure vessel) resulted in a much more significant loss of cellulose molecular mass, compared to oven drying under low conditions of relative humidity. The difference was attributed to a cessation of the hydrolysis once the paper became dry. To translate these results into practical terms, the humid environment of a paper machine can be expected to fall somewhere in between the extremes of wet-heating and oven drying. Gradual evaporation of water on the paper machine can be expected to keep the paper somewhat cooler, on average, than the dryer can surfaces, but the presence of high humidity will tend to keep moisture in the paper for a longer period, compared to oven-drying. Thus it is not possible, based on the present results, to rule out significant loss of cellulose molecular mass during drying of products composed of unbleached kraft fibers.

Mechanisms of Drying Temperature Effects

It is worth noting that the functions shown in Figs. 8-3 through 8-8 have a similar basic shape. One way to interpret this coincidence is to assume a common set of mechanistic causes of the changes in each of the measured properties.

The observed effects of drying itself, independent of temperature, appear to be most consistent with a capillary mechanism that has been proposed earlier by others [47]. Briefly stated, it is assumed that capillary forces act to close up pores in the fiber walls, and some of them fail to reopen. Thus, pore closure has been used to explain drops in either WRV [8, 11, 14, 17, 24, 48] or fiber saturation point determined by solute exclusion [4, 16], caused by drying of kraft or sulfite fibers. The same mechanism seems to be a likely explanation for the decrease in adsorption capacity of the fibers for poly-DADMAC. A possible alternative mechanism from the literature [34] involves the fibrils lying down irreversibly onto the fiber surfaces, reducing their tendency to interact with water. This alternative explanation appears less useful in the present case, since the refining level and external fibrillation were intentionally kept low.

The fact that further significant change in WRV, polymer uptake, and strength properties occurred with increasing drying temperature to levels above 150 °C [24] suggests that thermal softening of the structure may play a role. The glass transition temperatures of dry cellulose, hemicelluloses, and lignin have been reported as 200-260 °C, 150-220 °C, and 130-190 °C, respectively [49]. However, it is well known that the presence of water tends to plasticize these

polymeric materials, substantially reducing the glass transition temperatures [49-52]. Though such a softening mechanism probably is not required to explain results shown in Fig. 8-8, it is worth considering that increased molecular mobility may make cellulose more susceptible to hydrolysis. Further work is needed to confirm that the softening of the cellulosic materials under the given conditions of heat and moisture.

A practical concern associated with results shown in Figs. 8-3 through 8-7 is the expectation that drying conditions for such grades as linerboard, corrugating medium, and other paperboard grades will involve higher sheet temperatures and longer drying times, compared to lighter-weight paper products. On the one hand, the surface temperatures of the dryer cans tend to be higher during paperboard manufacture, due to the greater thermal resistance of the sheet. On the other hand, the greater thickness of board grades can be expected to limit the drop in temperature as the board passes between adjacent dryer can surfaces. The greater hot-wet incubation period implies that loss in WRV, a change sometimes called hornification [24], ought to be increasingly significant with increasing basis weight of similar products under otherwise similar furnish conditions. Another implication of these same trends is that “incubation” of paperboard between steel belts in a recently commercialized drying technology [52] might possibly affect WRV or pulp viscosity values to a different extent, compared to conventional drying.

CONCLUSIONS

1. Effects of drying of unbleached kraft fibers could be separated into two phases, one occurring in response to drying itself, irrespective of temperature, and a second phase resulting from exposure to drying temperatures of about 150 °C or higher. Cellulose viscosities, water retention values, adsorbed amounts of a cationic polymer, strength properties, and the apparent density of handsheets all followed similar trends. The results are consistent with the action of capillary forces during drying, with an additional softening effect at the higher temperatures.

2. Though some loss of fiber bonding potential appears to be unavoidable, within the parameters of conventional papermaking, the present work underscores the importance of avoiding the extremes of over-drying, especially if sheet temperatures exceed 150 °C.

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CHAPTER 9

Summary

The thesis research described in the preceding chapters showed, first of all, that drying of unbleached kraft pine fibers resulted in loss of cellulose viscosity, water retention value, fiber flexibility and capacity to adsorb poly-DADMAC from solution. Handsheets made from dried fiber had lower paper strength and lower apparent density, compared to corresponding primary handsheets made from never-dried fibers. With the increase in drying temperature of virgin fibers, the above properties of dried fibers or recycled handsheets experienced larger effects, especially for drying temperatures that exceed 150 °C.

Recycled handsheets had lower strength compared with virgin handsheets at all pH values considered during paper formation within the range of pH 3 to pH 8. There was no significant effect of pH on paper strength within this range. The lack of effect of sheet forming pH on paper strength implies that under practical papermaking conditions and for the kind of pulp considered in this work, adjusting sheet forming pH may be not an effective tool for increasing paper strength. The results from water retention value and cellulose viscosity measurements also supported this conclusion.

The fiber flexibility tests showed that the method is useful to determine the flexibility of individual fibers. Fibers were more flexible under alkaline conditions than those under acidic conditions. Fibers became less flexible with increasing salt concentration and hardness.

Adding lower molecular weight chemicals, such as glucose and sucrose, to never-dried fibers was found to improve strength of recycled paper compared to a control experiment, where there was no additional refining during recycling. Results from water retention value tests indicated that the sugar treatment protected the fibers from pore closure during drying. Fiber flexibility tests provided direct evidence that treated fibers had higher flexibility relative to untreated fibers. However, when refining was included in the recycling step, the treated and untreated pulps had the same increased recycled strength properties. Refining during recycling was able to restore the recycled paper to the same strength as paper made from the virgin fibers. Results from fiber flexibility tests indicated that fiber flexibility did not correlate with the recycled paper strength in the case where the fibers were further refined as part of the recycling process.

Certain high molecular weight polymers added to never-dried fibers were found to benefit the strength of recycled handsheets even at a low level dosage. This effect was attributed to residual chemicals being retained on fiber surface during recycling and working as dry strength agents as they did on the virgin fibers.

Based on the screening tests reported in this study, the following candidate treatments appeared most promising for maximizing the strength of recycled paper, or reducing the need for additional strength additives when paper is recycled: cationic starch, various other starch products, depolymerized guar

products, chitosan, and sequential addition of a cationic material and an anionic polymer such as carboxymethylcellulose (CMC).

Results showed that tensile strength and compression strength were affected differently by certain chemicals. Treatments favoring compression strength included many water-loving polymers, such as polysaccharide products. Treatments favoring tensile strength included chemicals having hydrophobic substituent groups.

CHAPTER 10

Future Research

This dissertation focused on various issues related to strength loss during recycling of kraft fibers, including effects of sugar treatment on the fiber properties and paper strength. Fiber flexibility and water retention value (WRV) are two of the main properties that were evaluated. Results suggested that fiber pore closure is a major factor responsible for paper strength loss during recycling. Since the change in fiber pores was determined by the WRV test, which only provided the change for total pores, it is realized that more fundamental work need be conducted to clarify the exact mechanism of paper strength loss due to drying through other techniques.

Inverse size exclusion chromatography (ISEC) seems to be an attractive way to measure the pore size distribution of the cell wall of fibers. With this technique, one would be able to make conclusions confidently whether sugars work as bulk agents to block pore collapse during drying. Some issues associated with this method are that the HPLC procedure and column packing need to be optimized for this application, and computer software is required to determine the elution time with high resolution.

Atomic force microscopy (AFM) is an important tool for the study of surface morphology and properties of materials. It is believed that using this technique will provide extra evidence to determine the effect of sugars on fiber pores. Additionally, a modified tip having hydroxyl groups would elucidate the issue of bond strength per unit of bonded area from a force-distance curve if one

assumes that the major of paper strength comes from hydrogen bonds that are existed between fibers. Since paper made from wet fibers, it makes sense that all tests should be conducted under aqueous conditions.

It is known that surface tension force makes fibers closer together when water is removed from the wet web. It is reasonable to expect that surface properties of fibers affect the fiber-fiber bonding. Thus it is of interest to know whether fiber become more hydrophobic or hydrophilic after sugar treatment. One way to explore the effect is to measure single fiber contact angle. It is found that the information can be obtained by using Wilhelmy technique that measures the dynamic wetting force of single fiber.

Although sugar treatment could benefit the strength of recycled paper, one should keep it in mind that this benefit might not be effective after the first cycle of papermaking because sugar has low affinity with fiber surface. Sugar will drain out during recycling processes. In order to improve the retention of sugar or lower molecular weight chemicals, a modification on chemical structure may be required, for instance adding a cationic group on such a chemical structure [1]. Future work should pay attention on this area.

An alternative way to improve the strength of recycled paper is to find new dry strength agents or strength programs. Since the technique related to polymer synthesis has been advanced in recent years, it is not surprising for the paper industry that a cheap and effective chemical will be developed to benefit both primary paper and recycled paper. It is noted that currently available dry strength agents have not been able to prevent pore closure during drying from

the results of water retention value tests. It is hypothesized that the candidate of such a polymer should have short, branched chains to help the polymer anchoring inside fiber pores to prevent the collapse of fiber pores.

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Appendix 1

Effect of Density on Paper Strength

Experimental Procedures

Primary handsheets: Refined unbleached kraft pine fibers (9000 revolutions with a PFI mill) were dispersed in a TAPPI disintegrator for 5 minutes before making handsheets following the TAPPI procedure except the pressing pressure with 10 psi and 30 psi respectively. The handsheets were dried in a TAPPI condition room for 48 hours before physical testing.

Recycled handsheets: Primary handsheets made at 30-psi wet pressing pressure were soaked in tap water for 6 hours before being dispersed in a TAPPI disintegrator for 5 minutes. The dispersed fiber slurry was to form recycled handsheets following the TAPPI procedure except the pressing pressure with 30 psi and 60 psi respectively. The handsheets were dried in a TAPPI conditioned room for 48 hours before physical testing.

Results and Discussion

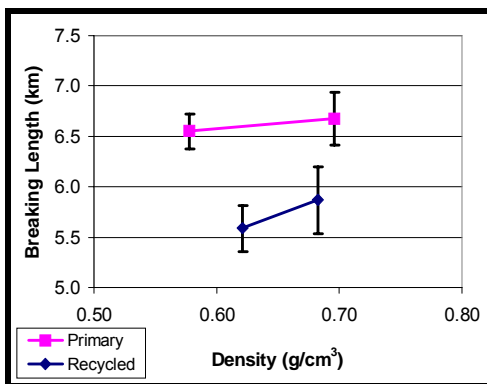


Fig. A1-1. Effect of density on breaking length

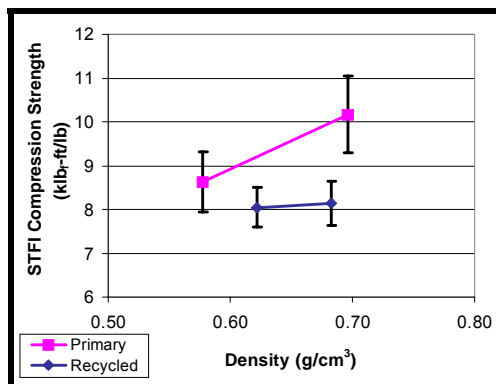


Fig. A1-2. Effect of density on STFI compression strength

Figures A1-1 and A1-2 show that increasing wet pressing pressure during making recycled handsheets cannot recover the loss of paper strength significantly. At the same level of apparent density, recycled handsheets had lower strength compared to primary handsheets. That meant that the effect of drying on paper strength could not be removed only through wet pressing alone during making recycled handsheets if one compares them under an equal apparent density.