The Effects of Heating Without Water Removal and Drying on the Swelling as Measured by Water Retention Value and Degradation as Measured by Intrinsic Viscosity of Cellulose Papermaking Fibers

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ABSTRACT

The effects of heating without water removal and drying of bleached kraft fibers were separately investigated. Water swellability as measured using a water retention value method (WRV) and cellulose degree of polymerization as measured using a viscosity method were used to gauge the effects of such treatments on fibers. The drying of fibers at temperatures above 100°C resulted in significant decreases in WRV, as expected. However, heating fibers without water removal at the same temperatures resulted in a decrease in WRV much less than caused by drying. Drying at high temperatures reduced the cellulose viscosity only slightly, whereas heat treatment without water removal at high temperatures resulted in much greater losses in cellulose viscosity. The results of this study indicate that the time-temperature-humidity history of a fiber during papermaking and paper recycling can produce fibers with very different papermaking qualities.

KEYWORDS

INTRODUCTION

It is well known that the use of cellulose fibers for papermaking results in changes to the fiber when compared to a virgin state. Fibers are subjected to a multitude of operations during the papermaking process that may affect the structure and properties of the fiber itself. It is generally accepted that chemically pulped recycled fibers display a decrease in papermaking potential as demonstrated through the formation of lower strength and lower quality products. Various studies have been performed to determine the cause of the changes that occur to fibers during papermaking.

Two important phenomena that occur during papermaking that can significantly impact fiber properties are (1) heating without water removal and (2) drying. For instance, in paper drying, the wet fiber web can be considered heated in the presence of water early in the drying operation (referred to as the heat-up zone) and then dried later in the operation (referred to as the constant drying rate and the falling drying rate zones). It is of interest to understand how these two phenomena affect fiber swelling and pore behavior as well as fiber strength and the condition of cellulose within the fiber.

Fiber Swelling and Recycling

One pronounced change in chemical pulps after recycling is a loss in fiber swelling [1,2]. Much of the strength loss in previously dried paper relative to virgin paper has been attributed to reductions in the swellability of the fibers. Decreases in swellability are thought to cause a loss in wet fiber flexibility and a resulting decrease in relative bonded area (RBA) of the sheet formed from them [1,3,4]. A commonly used measure of fiber swelling is the water retention value (WRV)[1]. The WRV measurement is used to determine the amount of water retained in a fiber when it is subjected to a certain amount of centrifugal force. This can be interpreted in terms of mainly the accessible pore volume, but is also affected by the fiber surface properties. This technique does not separate the effects of changes in the fiber surface from changes in the pore volume or accessibility of a fiber surface to water. The WRV value of fibers has been correlated directly with the strength of a sheet formed from the fibers [5,6]. This follows from the concept that water absorption increases when the fiber wall is delaminated, which in turn increases the fiber’s flexibility and bonding potential.

Another method that has been used to characterize fiber swelling is the solute exclusion method [7] by which solute molecules of various sizes are used to approximate fiber pore sizes and the amount of water retained therein. While it is agreed that the solute exclusion technique is accurate at determining the total pore volume, it has been suggested that conclusions regarding pore size distributions should be regarded with some caution [8,9].
In agreement with the concept that the reduction in swelling reduces the flexibility of recycled fibers, fibers have been found to suffer a reduction in wet flexibility after repeated recycling [10]. Work by Jayme [1] in the area of WRV measurements indicated that fibers show a decrease in WRV after initial drying. Air-drying and heat-drying have both been shown to reduce the WRV of fibers, and the intensity (varied through time and temperature) of the drying influences the extent of WRV loss [5,11,12,13]. The decrease in WRV upon removal of water is most pronounced upon the first drying; subsequent wetting and drying cycles have much smaller effect.

By examining fiber cross-sections, another study found that fibers shrink and become denser after air drying and reslushing [12]. A model for the reduction in swelling capacity involves the bonding of microfibrils during drying such that the pores between the microfibrils are no longer accessible to water molecules [7].

**Pores in the Cell Wall and Drying**

The reduction in fiber swelling upon drying has been partly attributed to reductions in the pore volume of fibers during drying [14]. Studies have indicated that there are significant changes in the pore structure of fibers during drying, some of which are reversible by reslushing in water, and some of which are not. Using a solute exclusion method, Stone and Scallan [14] found that the reduction in internal pore volume begins at approximately 50% moisture, and that irreversible pore volume reduction ceases at about 40% moisture. This indicates that removal of water from the fiber beyond about 40% moisture causes closure of internal pores that reopen upon rewetting. The difference between reversible and irreversible pore closure must be dependent upon the bonds formed during processing and the accessibility of these bonds to water or other solvent.

If a pore is closed and does not reopen upon soaking in water, the bonds formed between adhering surfaces must be either covalent or crystalline in nature, or the surfaces must be in such close contact that water does not penetrate between the surfaces. Whether the bonds formed are impenetrable due to their covalent nature or to the reorientation of microfibrils during co-crystallization is unknown. Significant evidence exists to suggest that hydrogen bonding plays an important role in the loss of swelling after drying. Work by Sumi et al. [15] has shown through deuterium exchange and infrared analysis that drying cellulose reduces the accessibility of hydrogen bonds to water within the cellulose. It has been suggested that the permanent closure of pores causes hydrogen bonding that is stronger than the hydrogen bonds present in an undried fiber, due to the orientation of cellulose crystallites [16]. This irreversible change in pore structure has also been attributed to reorientation and recrystallization of the crystalline structure of cellulose [16]. Several researchers have reported increases in crystallinity of pulps upon multiple recycling, or moderate and accelerated drying [17,18]. In contrast, X-ray diffraction [19] and NMR [20] did not detect changes in the extent of crystallinity of fibers upon drying.

Stone and Scallan [14] also observed variability in the extent and reversibility of pore closure from the exterior to the interior of a fiber. It was speculated that pores near the surface of the fiber close first, and that these pores, once closed, are more difficult to reopen. Also, the changes in pore closure that accompanied drying of the fibers were dependent upon whether the fibers were air dried or dried under heat. When subjected to drying at elevated temperatures, the median pore size decreased, whereas it did not decrease for air dried pulp. Such a discovery leads to the suspicion that different mechanisms influence the closure of pores in air drying versus heat drying. If such was the case, the added heat treatment, separate from the removal of water, would impart specific changes to the structure of the fiber.

Another study [7] indicated that pore closure was dependent upon the size of the pore itself, and that the smallest pores did not close during drying, while the largest pores were most affected by drying. Allan and Ko [21] explained their finding that the smaller pores do not close as readily by modeling the various forces acting upon pores during water removal and in a static, never dried state. These forces include the effects of the potential energy of attraction between colloidal particles, the repulsive effects of overlapped electric double layers between lamellae, and the effects of water tension in a meniscus formed during water removal. If this pore closure was caused by water tension effects, as often speculated, then the effects of the said water tension induced pore closure would be manifested differently in different pore sizes. This would be indicated by differences in closure of pores of different sizes, because smaller pores would experience greater surface tension forces pulling the pores together. Results indicated that the pore size distribution closely resembled that predicted by the proposed theory of surface interactions [21].

**Studies Involving Heating With and Without Drying**

The effect of heating fibers without drying has been investigated in order to separate the effects of water removal and heat treatment. By boiling pulp suspensions, heating alone without drying was shown to decrease the swelling and water uptake of fibers [11,22]. Other research has shown that thermal treatment of pulp in water results in increases in crystallinity [23,24]. Stockman and Teder [25] found that pulps heated above 120°C before formation into handsheets showed lower tensile strength than sheets formed from untreated pulps. Also, in that same study
heated pulps required increased refining in order to reach comparable strength to an untreated pulp. This observation suggests that some sort of change in the fiber renders it less susceptible to defibrillation by mechanical means. This indicates that water removal alone does not account for all of the strength losses in heat dried pulps, and that the portion of time in which the fiber is heated in the presence of water may also cause reductions in the papermaking potential of fibers. However, it was also found [26] that pulps heated after beating did not suffer the same relative strength losses compared to pulps heated before beating. This indicates that the detrimental effects of heating do not affect a fiber that has been refined immediately before and is in an already highly swollen state.

Heating without water removal has also been found to affect the fiber strength. Stockman and Teder [25] found that bleached sulfate pulp heated above 120°C in the presence of water became brittle, reflected in the observation that the freeness of the pulp was unacceptable after refining to a desired tensile strength. This embrittlement of the fiber was speculated to be caused by a consolidation of the cell wall. Horn [27] found a reduction in fiber strength, as measured by zero span tensile, upon multiple sheet recycling processes.

Klungness and Caulfield [28] found that accelerated aging of paper at high temperatures and 50% RH led to large decreases in the degree of polymerization (DP), as reflected by decreases in pulp viscosity. However, drying of the pulp to zero moisture content at high temperatures resulted in only minor DP reductions. Another report [5] indicated that bleached pulps treated under saturated conditions at temperatures greater than 150°C suffered significant losses in cellulose DP, with higher temperatures and longer treatments increasing the magnitude of DP decrease. Unbleached pulps were unaffected by equivalent treatments.

**Motivation**

Previous work in the area of cellulosic based fiber processing has indicated that drying and heating without water removal both affects the fiber properties important for papermaking. Both of these processes occur during paper drying, a complicated process in which water removal, heating in the presence of water, and heating in the absence of water all occur. In a previous report [29] it was shown that drying of bleached and unbleached fibers resulted in decreased swellability of the fibers, with larger decreases observed as the drying temperature increased above 120°C. The drying temperature caused decreases in the pulp viscosity of unbleached fibers, but not of bleached fibers. The difference in the relationship between drying and viscosity between unbleached and bleached fibers was explained by showing that the degree of polymerization decrease (in percentage terms) is statistically sensitive to the initial degree of polymerization of the cellulose.

There still is a need to better define the separate effects that are caused by heating without water removal and water removal at the same temperatures. This study has as its objective to clearly define the impact that heating without water removal and water removal have on fiber properties versus temperature. The analysis of fiber properties will be based on two common measures of fiber quality: fiber swelling as measured by water retention value (WRV) and fiber degradation as measured by cellulose viscosity. This is important to be able to determine what processes affect the papermaking potential of fibers and how these changes occur in the fiber. Once the causes and effects of different operations are known, it may be possible to reduce, adjust, or eliminate the detrimental effects of the operations in order to maintain the properties of a given pulp for purposes of recycling or dry lap pulp use.

**EXPERIMENTAL**

Previous authors have noted greater effects of heating and drying on bleached pulp relative to unbleached [28]. Therefore, to have the largest expected differences due to heating or drying, a bleached softwood kraft pulp was obtained from a typical kraft pulp mill in the Southeast United States for our experiments. The pulp had a pH of approximately 6, and was obtained at approximately 10% consistency, having never been dried. In order to separate the effects of water removal and heating, a general experimental layout was used as outlined in Figure 1.

This scheme provides pulps that have been air dried with no heat treatment, heat dried to zero moisture content at
varying temperatures, and heated without drying at various temperatures. This terminology will be used throughout: air drying means drying at controlled conditions of 23°C and 50% R.H. for over 24 hrs; heat drying means drying with uncontrolled evaporation for fifteen minutes; heating means heating under pressure and saturated steam conditions for fifteen minutes, without removal of water. PFI refining was performed on 30 OD (oven dried) gram samples at 10% consistency for either 3000 or 6000 revolutions (about 2 and 4 minutes respectively). For all trials, handsheets (2 OD gram) were prepared on a standard handsheet mold, with no recirculation. The sheet was covered with three sheets of blotter paper, rolled three times with a weight in order to aid in the removal from the mold, and then transferred to a TAPPI standard press; only the first pressing cycle was used. This gave an applied pressure of 50 psi (345 kPa) for 5 minutes, and yielded a consistency of about 30%. The sheets were then transferred to metal plates and placed and standard metal drying rings, restrained by tightening the screws and compressing the rings, and then subjected to each respective treatment process.

For air drying (AD), the sheets in the rings were left to dry overnight at controlled conditions of 23°C and 50% RH. For heat drying, the sheets in the rings were placed in laboratory oven at the specified temperature for 15 minutes, then cooled for 5 minutes in the open atmosphere before being sealed in plastic bags. Sheets that were subjected to heat treatment were placed between two metal plates and tightened in the rings. They were then placed in a laboratory high-pressure digester. The digester was fed with saturated steam at approximately 140 psi (970 kPa) until the temperature reached the desired setpoint. The total treatment time was 15 minutes, after which the digester pressure was relieved, and the sheets were removed from the digester. The sheets were then cooled for 5 minutes in open air and transferred to sealed bags for cold storage.

After treatment, the sheets were tested for 0.5 % Cupraethylenediamene (CED) viscosity and water retention value (WRV). Samples tested for viscosity were conditioned for 24 hours at 23°C and 50% RH. This process air-dried the samples that had been heated, and allowed moisture uptake by the sheets that were heat dried. The samples were then tested for viscosity according to TAPPI T 230 om-89. Samples were tested for WRV by using a modified version of TAPPI UM 256. Small samples of the pulp were dispersed in deionized water in a British Disintegrator (3000 rpm, 5 minutes, 1.2% consistency, and 2000 grams total) then allowed to soak for 24 hrs. The samples were then formed into pads on a no. 4 Fisher filter paper and dewatered to approximately 25% solids. Samples of the pad were weighed and placed in sintered centrifuge tubes (pore size 22 mm, volume 3 mL, provided by MSI). The samples were then centrifuged at 900 g, for 30 minutes.

After centrifuging, the samples were removed from the tubes, weighed, oven dried, and weighed again. The WRV was calculated as the sample weight after centrifuging minus the OD weight (i.e., the weight of water after centrifuging) divided by the OD weight.

RESULTS AND DISCUSSION

The Effect of Drying on Water Retention Value

It has been noted that refining causes an increase in never-dried WRV, which is accompanied by a greater decrease in the papermaking potential of the dried fibers. Freeness decreased with increased refining as expected and as shown in Table 1.

<table>
<thead>
<tr>
<th>Level of Refining in PFI Mill</th>
<th>Average Canadian Standard Freeness, mL</th>
</tr>
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<tbody>
<tr>
<td>0 Revolutions</td>
<td>690</td>
</tr>
<tr>
<td>3000 Revolutions</td>
<td>580</td>
</tr>
<tr>
<td>6000 Revolutions</td>
<td>440</td>
</tr>
</tbody>
</table>

It is known that refining causes delamination and defibrillation of the cell wall, which in turn allows greater accessibility of water within the fiber. This raises the WRV of the fiber [30]. A 15% increase in the WRV of never-dried fibers refined for 6000 revolutions in the PFI mill relative to unrefined fibers is observed in Figure 2. This observation is in accordance with published results [30,31]. A similar increase in WRV is observed with increased refining even for air-dried samples. However, it is also seen in Figure 2 that air drying decreases the WRV of the pulps at all levels of refining relative to the never-dried pulp by 12-14%. Jayme

![Figure 2. Water Retention Value of fully bleached chemical pulps versus refining level for never dried and air-dried chemical pulps. Trend lines for never dried (solid line) and air dried (dashed line) WRV are shown.](image-url)
[1] found a 34% decrease in the WRV of unbleached sulfite fibers upon air drying, and de Ruvo and Hutn [5] found that the WRV of refined fibers decreased approximately 25% after drying, to a value near that of the unrefined never-dried fibers.

The effects of heat drying at the three levels of refining and three drying temperatures are shown in Figure 3. The temperature of the heat drying (125, 150 or 175°C) does not appear to be a significant factor in the WRV. Heat drying of fibers at all temperatures above 125°C caused an average of 38% decrease in WRV compared to never dried fibers at similar levels of refining. The heat dried fibers exhibited an average of 22% lower WRV at similar levels of refining than the air dried fibers. The result that drying at elevated temperatures further decreases WRV relative to air drying has also been shown in the study by de Ruvo and Hutn [5] and by this research group [29], although it was not performed at multiple levels of refining. Similar to the results herein, de Ruvo and Hutn [5] observed that the effect of drying at elevated temperature on WRV was generally independent of the drying temperature.

There appears to be no relationship between the refining level and the WRV, Figure 3. This finding indicates that increased refining before drying at elevated temperatures does not result in additional decreases in WRV. Previous research [3] has indicated increased hornification during drying upon increased initial refining of a pulp, but this was measured by decreases in strength properties and not WRV, although the two are often related.

The Effect of Heating Without Drying on Water Retention Value

In order to separate the effects of heating from drying, it was of interest to examine the effects of heating undried fibers to elevated temperatures without water removal. This was accomplished by subjecting undried fibers to elevated temperatures at pressures great enough to prevent boiling of the water. Figure 4 shows the effects of heating without drying on bleached kraft fibers. Samples that were heated without water removal displayed a lower WRV than air dried samples and a significantly lower WRV than samples not dried. However, the samples heated without drying had higher WRV than samples dried at high temperature. No significant relationship between refining or heating temperature and the WRV was discernible from the data in Figure 4.

In general, refining before heat treatment resulted in somewhat higher WRV when compared to unrefined fibers, but this can only be based on the average WRV for the different heating temperatures at each refining level. This is consistent with the findings for dried fibers, and confirms the observance that refining before treatment did not reduce the WRV after treatment below that of unrefined fibers.

Discussion of Decrease in WRV with Heating and Drying

These results indicate that heating without drying decreases the WRV of fibers, but not to the same extent as heating with water removal. These results indicate that heating, separate from or in combination with, water removal plays some role in the hornification of wood pulp over the temperature range studied. Thus more than one mechanism for WRV loss may be acting on the fiber during heat drying; this would explain the high degree of WRV drop in heat dried fibers. One aspect of the process is induced by heat, whereas another requires water removal. The water removal
is assumed to mechanically close pores within the fiber, whereas several theoretical mechanisms may act through heat to change a fiber’s ability to hold water. Among these is that heating in the presence of water helps release stress in the fiber wall and reorients cellulose chains, increasing crystallinity. The removal of hemicelluloses or the migration of extractives to the surface (for unbleached fibers) has also been indicated [32].

Decreases in WRV are expected to involve either insoluble bond formation between the microfibrillar surfaces of the fiber pores, or a reduction in the affinity for water of the surfaces of the fiber [5]. When fibers are dried freely, water tension forces in combination with colloidal attraction forces dominate pore closure [30]. Since pores that do not open upon rewetting cause decreases in WRV measurements, the pore closure measured by decreases in the never dried WRV must be accompanied by bonds that are not broken upon soaking in water. The water absorption capacity of the fiber may also be reduced by removal of hemicelluloses [22, 26, 32], or by inactivation of the fiber’s surface, which restricts its ability to hold water [33]. Studies by de Ruvo and Htun [5], however, have shown that structural pore closure is a major component in the hornification of fibers at elevated temperatures.

It is of significant interest how fiber treatments affect the reversibility of pore closure. Once the surfaces of two lamellae have come into such intimate contact as to constitute pore closure, several possible bonding scenarios may occur. If the surfaces are within 1 to 5 Angstroms, and the proper chemistry and orientation occur, hydrogen bonding becomes possible [34]. Proposed mechanisms for non-water soluble bonding in pore closure include cellulose crystallization, ‘strong’ hydrogen bonding, and crosslinking between lamellae. If cellulose chains in the amorphous region are mobilized by water absorption, then mechanical action and water removal may cause a reorientation of cellulose crystals, thus making bonded microfibrillar surfaces impervious to water. Even if the majority of the surfaces are bound by soluble hydrogen bonds, the close contact of any two surfaces that prevents the entry of water into the swellable region of the fiber may cause irreversible decreases in the pore volume by preventing water from accessing the soluble bonds within. Thus a small amount of water-insoluble bonding within a fiber may close pores and prevent swelling.

Hydrogen bonding has been shown to play an important role in the hornification of fibers [15]. If a hydrogen bond is accessible to water, the bond may be disrupted, as can be seen upon the wetting of paper. Pores closed by hydrogen bonding would open upon wetting, unless some mechanism was acting to reduce the accessibility of these bonds to water molecules. The fact that crystalline cellulose is insoluble in water, and starch is soluble in water despite nearly identical chemical structures [35], illustrates the effect of ‘strong’ hydrogen bonding on the solubility of certain bonds in water. Thus, the structure and organization of cellulose chains within a fiber’s pores are of great importance in determining the accessibility of the pores to water. It has been suggested that cellulose recrystallization through partially irreversible hydrogen bonding between cellulose chains may be responsible for the restriction of swelling that accompanies hornification [36]. An increase in the hydrogen bonding between cellulose chains in the amorphous region may also take place, even if the change is not detectable as an increase in crystallinity [20,37]. However, in order for the previously unbonded cellulose chains or crystallites to bond, there must exist significant mobility in the cellulose chains so that the proper geometry and distance may be achieved by the bonding molecules. The kinetic energy of a molecule increases with increasing temperature [38], and the presence of a potential solvent increases molecular mobility. Thus, the cellulose molecules would be more mobile during the heating without drying phase. This supports the observation that temperatures at and above 125°C decrease the swellability of fibers, regardless of whether they have been dried. Also, the presence of water within the fiber walls may be important for crystallization and reorganization. These conditions are consistent with the findings presented here that the presence of water in combination with heat causes losses in WRV, even if water is not removed from the fiber.

Another proposed mechanism for irreversible pore closure involves chemical bonding of cellulose microfibrils through crosslinking [39,40]. Oxidation of celluloses and hemicelluloses to form carbonyl groups has been shown to lead to the formation of covalent hemi-acetal type bonds between cellulose chains [41]. The same author suggested that the crosslinking reactions are dominant when there is little moisture present within the fibers. Even a small degree of crosslinking within the pores of a dried fiber may reduce swelling by creating irreversible bonds that prevent water from entering the pore in order to re-swell the pore. Additionally, the bonds formed are covalent in nature and thus are not easily broken when the fiber is dispersed in water.

It is also important to note that any degradation of the cellulose molecule (as elucidated in the next section) may result in additional functional groups that may take part in a crosslinking reaction.

**Cellulose Degradation**

The degree of polymerization (DP) of bleached softwood kraft market pulp as reflected by cellulose viscosity was used to measure the effects of heating and drying. Cellulose DP is directly related to the intrinsic viscosity by the Mark-Houwink Equation [42]. The effect of drying for fifteen
minutes at different temperatures is shown in Figure 5. It has been reported and is assumed herein that air drying at 23°C for 24 hours does not cause any degradation of the cellulose [5]. Thus, these findings indicate that the drying of the pulp at high temperatures did not significantly decrease the viscosity, similar to our previous results [29]. Klungness and Caulfield reported a 31% decrease in viscosity of bleached pulps after drying on a hot plate at 140°C [13]. It should be noted that the photographic drying process used in that study differed from the oven drying treatment used in the present study, of particular note, the final moisture was always greater than 2% (higher than the negligible final moisture content from the convection oven drying in this study).

The viscosity values for samples heated without drying are shown in Figure 6. Also plotted is the average viscosity for all of the samples that had been dried (average from data from Figure 5). The samples heated without drying experienced significantly decreased viscosity relative to the dried samples. The viscosity reduction for heated samples also increased with increasing temperatures. A 56% decrease in the viscosity relative to the dried samples was observed for heating to 175°C. This is in agreement with findings of Klungness and Caulfield in which dried sheets were treated at high temperature and 50% R.H. for extended periods of time [13]. Also, Stockman and Teder reported a decrease in viscosity of about 40% upon heat treatment under saturated conditions for five minutes [25].

**CONCLUSIONS**

Heating without water removal and drying were observed to result in different changes in fibers upon treatment.
Heating fibers without water removal decreases the WRV of fibers but not to the same extent as drying the fibers. This indicates that heating, separate from water removal, is responsible for some portion of the hornification of fibers. Drying at high temperatures does not significantly reduce the cellulose viscosity (degree of polymerization), whereas heat treatment without water removal at high temperatures results in significant losses in viscosity. These results confirm that the temperature and moisture history of a fiber in any processing operation can have an impact on the papermaking potential of recycled fibers.

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