CELLULOSE MICROFIBRIL-WATER INTERACTION AS CHARACTERIZED BY ISOTHERMAL THERMOGRAVIMETRIC ANALYSIS AND SCANNING ELECTRON MICROSCOPY

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Microfibrillated celluloses, liberated from macroscopic lignocellulosic fibers by mechanical means, are sub-fiber elements with lengths in the micron scale and diameters ranging from 10 to a few hundred nanometers. These materials have shown strong water interactions. This article describes an investigation and quantification of the 'hard-to-remove (HR) water content' in cellulose fibers and microfibrillated structures prepared from fully bleached softwood pulp (BSW). The fiber/fibril structure was altered by using an extended beating process (up to 300 minutes), and water interactions were determined with isothermal thermogravimetric analysis (TGA). Isothermal TGA is shown to be a convenient and insightful characterization method for fiber-water interactions for fibers and microfibrils at small sample size. In addition, scanning electron microscopic (SEM) images depict the differences between fibers and microfibrils with respect to beating time in the dried consolidated structures. Highly refined pulps with microfibrils were determined to have two critical drying points, *i.e.*, two minima in the second derivative of weight versus time, not before reported in the literature. Also in this study, hard-to-remove (HR) water content is related to the area above the first derivative curve in the constant rate and falling rate drying zones. This measure of HR water correlates with a previous measurement method of HR water but is less ambiguous for materials that lack a constant drying rate zone. Blends of unbeaten fibers and microfibril containing samples were prepared and show potential as composite materials.

INTRODUCTION

Microfibrillated cellulose (MFC), a special class of cellulosic materials, was first developed by Turbak *et al.* in 1983 from purified cellulose fibers using wood pulp as starting materials (Turbak *et al.* 1983). MFC is basically a material produced by disintegration of cellulosic fibers by high pressure mechanical homogenization into sub-structural fibrils and microfibrils possessing lengths in the micron scale and widths ranging from 10 to few hundred nanometers (Spence *et al.* 2011). A wide variety of fiber sources have been used to prepare MFC, including primarily woods, agricultural crops

and by-products, bacterial cellulose, *etc*. Depending upon the source of raw material and the degree of processing, extensive mechanical defibrillation (*e.g.,* refining and high pressure homogenization, grinding, cryocrushing) is also combined with chemical treatments (*e.g.,* alkaline pretreatment, oxidation pretreatment) to produce purified cellulose. In some cases, enzymatic pre-treatment is used to reduce the energy requirement. A more detailed description on the microfibrillated cellulose preparation can be found in a recent review article on microfibrillated cellulose preparation and their use in nano-composites (Siró and Plackett 2010).

Characterization of water associated with cellulose fiber-water system in regard to its thermodynamic (Stone and Scallan 1967; Maloney and Paulapuro 1998a; Driemeier *et al.* 2012), molecular dynamics (Menon *et al.* 1987), and solution properties (Stone and Scallan 1968) has been a subject of interest. The presence of different pore sizes within the fiber play an important role in determining the type of interaction between the water and the surrounding macromolecules (Hubbe *et al.* 2009).

Recently, Spence *et al*. (2011) reported a comprehensive investigation on MFC production from a variety of raw material sources using different mechanical processing techniques. A thorough investigation of the microfibril-water interaction revealed that the water retention value (WRV) for MFCs from raw materials were in the range of 4.5 to 30 g/g, depending on microfibril's chemical composition. The water vapor transmission rates (WVTR) for MFC films produced from microfibrils with varying chemical composition were in the range of 2.0 to 5.1×10^{-2} (($g/m^2 \times day$)/m), with an initial water contact angles of 48.2^o to 88.1^o, and water adsorption in the range 2.3 to 3.2 g/g (Spence *et al.* 2010a).

Accordingly, the strong interaction among cellulose fibers (or fibrils) and between water and cellulose fiber directly affects the thermodynamics of the water removal from cellulose fiber (Liu and Yao 2001; Nakamura *et al.* 1981; Ping *et al.* 2001). The removal of water during the drying process is an important subject of interest for many industries, *e.g.* paper, textiles, agriculture, food, and pharmaceutical industries. In the paper industry, cellulose fiber-water interaction is an important parameter that controls the final physical properties of paper and the process economics in terms of drainage rate, press solids, and drying energy (Back 1978; Hubbe *et al.* 2007). A small change in moisture content, which is further reduced by the repetition of drying and recycling of fibers, can significantly affect the final strength of paper and paperboard products (Bobalek and Chaturvedi 1989; Bovin *et al.* 1973).

Another important factor, the process economics, is also reliant on the final drying of the paper or paperboards. Generally, during the paper making process most of the water is removed by mechanical action, because mechanical dewatering is much cheaper than thermal dewatering. However, to achieve a final solids content of about 95%, thermal drying of a paper web in the final stage is necessary.

Although the dryer section is responsible for only a small amount of the total water removal, it is the major energy consumer in the paper mill. Moreover, the dryer section is the final processing stage that determines the strength and absorbent properties of paper products. Energy consumption during the drying of paper and paper board products can be understood by the hygroscopic and porous structure of pulp fibers that contain hard-to-remove water.

As the beating time increases, energy consumption in drying will also increase due to the increased amount of hard-to-remove water (Park *et al.* 2007a,b). Hence, a deep understanding of the interaction between cellulose fibers/microfibrils and water is required.

In the pulp and paper industry, the level of refining, swelling, and mechanical properties of fibers and papers are correlated to their corresponding WRV and freeness value (Scallan and Carles 1972). WRV is defined as the ratio of water to dry fiber after centrifugation of a fiber pad under standard conditions and is used as a measure of fiber swelling. Fiber swelling, which emphasizes the inter-fiber bond development in paper, is directly associated with the degree of fiber flexibility and fibrillation. Another parameter, the freeness, is a measure of the water drainage rate from a fiber suspension under controlled conditions. Freeness measurement is used as an indicator of drainablility on the paper machine, and as a process-monitoring tool for refining to develop paper strength. Despite their conveniences, there seems to be lack of scientific implications of these methods (Abson and Gilbert 1980; Clark 1970). Further, WRV and freeness measurements require about 0.5 and 3 g of dry fiber mass, respectively. Although these amounts of dry fiber are relatively small in the case of papermaking standards, these sample sizes are considered as large in the case of sample fibers extracted from genetically modified trees grown inside greenhouses (Park *et al.* 2006a).

Other methods to characterize absorbed water are available. Nakamura *et al.* introduced a method based on differential scanning calorimetry (DSC) to quantify the sorbed water into the polymer (Nakamura *et al.* 1981; Weise *et al.* 1996; Maloney *et al.* 1998). Another instrumental technique, nuclear magnetic resonance (NMR) spectroscopy to measure the sorbed water into cellulose was initiated by Odajima *et al.* (1959). Later, this technique found application to characterize and quantitatively measure the bound water in a fiber-water system (Ogiwara *et. al.* 1969; Froix and Nelson 1975; Topgaard and Söderman 2002). All of these methods categorized the sorbed water in fiber into three different classes *e.g.*, unbound, freezing bound, and non-freezing bound water based on the thermodynamics of the water associated with cellulose fibers. However, these techniques are not very practical because of significant operator training needed to operate and to interpret the data with expensive equipment.

In an earlier publication, a simplified and convenient method to determine the hard-to-remove water content was developed using high resolution thermogravimetric analysis (TGA) (Park *et al.* 2006a). Fiber samples were prepared from bleached softwood kraft pulp after beating, using up to 4.5 kg load and beating time up to 40 minutes. Observed drying kinetics revealed three different drying regimes: warm-up zone, constant rate zone, and falling rate zone. After placing a wet fiber sample inside the TG furnace, initially the drying rate increases as the sample warms up; this regime is considered as the warm-up zone. After warming up, the evaporation rate of water from the fiber remains relatively constant up to a point. This zone has been assigned as the constant rate zone. The constant rate zone over a wide range of time is a manifestation of a constant water evaporation, which is originated from the constant movement of moisture from the interior to keep the exposed surface 'sufficiently wet' (Belhamri 2003; Schlünder 2004). After the constant rate zone, a prolonged exposure to the isothermal condition leads to a decrease in the drying rate. This is the beginning of the falling rate zone. The moisture ratio at the onset of this decrease is considered to be related to the fiber characteristics. This isothermal TGA protocol can simply be utilized to identify different classes of water in fibers and then predict the drying behavior of fibers.

In the current study, an isothermal TGA was used to investigate sorbed water present in fibers and microfibrillated cellulose prepared from bleached softwood kraft pulps after beating for extended times (up to five hours). The different drying regimes of fibers with and without heavy refining were characterized using TGA. However, for highly beaten pulps containing microfibrillated cellulose the distinction between the falling rate zone and the constant rate zone becomes very difficult to determine, and an alternate measure of water interaction is proposed herein. In addition, SEM image analysis was performed to analyze the fiber/microfibrillated cellulose samples and consolidated dried material structure at different degrees of beating.

EXPERIMENTAL

Sample Preparation

Fully bleached commercial kraft softwood pulp (moisture content of about 8%) was used for all experiments. Eleven samples were produced with different beating times using a valley beater at 1.5% consistency with pre-soaking for three hours. Initially, the valley beater was run for 20 minutes without any load to fiberize the pulp sample. Then, samples (one liter) were collected after every 30 minutes with a maximum beating time of five hours with a load of 5 kg. The samples were stored in cold storage at 4 ^{o}C until further use.

Methods
Fiber quality analyzer

A Fiber Quality Analyzer (FQA) LDA96 (OpTest Equipment Inc., Ontario, Canada) was used to determine the fiber length and fines content. A quantity of sample (about 1 mL) was taken from the refrigerated sample and added to 600 mL of deionized water. The instrument measured the properties of over 3000 fibers per sample. Percentages of fines measured in this study are the length-weighted percentage of fines. This is an estimate of the weight fraction of the fines, assuming that the coarseness is constant for all length classes. A fine is defined as any object having its largest dimension shorter than 200 micrometers. The FQA classifies an object as anything longer than 70 micrometers. The reported mean length in this study is the length-weighted average of detected fibers. This value is most often used to compare differences between samples. Fines tend to have a minor effect on this result under normal conditions. The length-weighted average can be calculated from,

$$L_w = \sum n_i L_i^2 / \sum n_i L_i \qquad (1)$$

where L is the contour length and n is the fiber count in the ith category.

This formula shows that by squaring a term the contribution of the term becomes larger for large terms and smaller for small terms. Other data such as curl index and kink index and arithmetic average width were also determined.

Thermogravimetric analysis

A volume of 100 mL of sample with 1.5% consistency was taken and mixed with 200 mL of deionized water. With house vacuum on a Büchner funnel, a handsheet was made on a filter paper. When no more water could be removed by vacuum, the sheet was

separated from the filter paper and divided into two parts. The first part was introduced into an oven to evaluate the consistency of the sample, and the other part was stored in a refrigerator in an air-tight aluminum container. Some amount of the wet sheet was mixed with deionized water to produce a consistency of 9.1% (10 g water /g OD fiber). Then a 100 mg wet sample was introduced into the furnace of a thermogravimetric analyzer (TGA Q500, TA instruments, New castle, DE). A platinum sample pan (Part #952018.906, TA Instruments) was used to hold the sample, as specified by the previous study (Park *et al*. 2006a). The sample pans have a dimension of 2 mm height and 10 mm diameter. The drying experiments were run at an isothermal temperature of 90 °C until no more drying occurred, about 45 minutes. Dry nitrogen gas was used at a flow rate of 40 mL/min for balance gas and 60 mL/min for sample gas. Drying was defined as complete when the weight percent loss per minute was less than 0.001%/min.

SEM analysis
        Two methods of sample preparation were used for SEM analysis. First, handsheets were made on filter paper using a Büchner funnel and house vacuum. The sheets were removed from the filter paper, placed within two plastic restraining rings, and clamped tightly. The samples were allowed to dry in a controlled environment, 23°C and relative humidity of 50%. SEM analysis was performed on the side not contacting the filter paper. Second, a very dilute suspension of about 10 mL of sample was placed into a small glass tube and freeze-dried for at least 18 hours. A low-density pad of dried fibers was produced. A Hitachi S3200 N scanning electron microscope at 5kV with a resolution of 1600 x 2000 pixels with different magnification was taken. Samples were secured onto carbon tape and then kept inside the vacuum chamber (containing the microscope) during the collection of images.

Blending procedure
        TGA and SEM experiments were also performed with blended samples. Samples with 0 hour beating time and 5 hours beating time were used for this purpose. Blended samples used were 100/0, 80/20, 50/50, 20/80, 0/100 mass ratio of sample with no beating/sample with 5 hours beating. Blends were produced by adding the proper ratio of samples to produce a volume of 100 mL at 1.5% with 200 mL of deionized water and then stirring the samples vigorously. A pad was made using a Buchner funnel with house vacuum and a consistency was measured. TGA and SEM analysis were performed following the same procedure as non-blended samples described above.

RESULTS AND DISCUSSION

Effect of Beating on the Fiber Properties
        It is well known that beating affects fiber quality significantly by cutting of fibers, delaminating of lamellar structure, flattening of fiber and lumen, and promoting swelling within the fiber wall (McIntosh 1967; Page and De Grace 1967). This results in swollen and flexible fibers that make strong paper, but at the expense of some reduction of the fiber length (Claudio-da-Silva *et al*. 1982). The length-weighted average length decreased, and the length-weighted percentage of fines (<0.2 mm long) increased with respect to the beating time for the softwood pulp, as shown in Fig. 1. Two beating runs were performed, and the results were found to be reproducible. The width of the fiber

fraction decreased slightly upon beating from about 30 microns to about 25 microns for beating at 5 hours. The curl and kink indexes were basically constant at around 0.15 and 1.5, respectively. It is important to mention that from Fig. 1 it was observed that prolonged beating of fibers of more than 210 minutes was required to convert the fibers to their corresponding microbril materials when length-weighted average length becomes less than or about 200 microns. Normal beating times to prepare wood pulps for papermaking are less than 60 minutes for bleached softwood pulps (T 200 sp-96, 2000). Beating times greater than 90 minutes would be uncommon for papermaking, resulting in unacceptably high fines content and poor drainage properties.
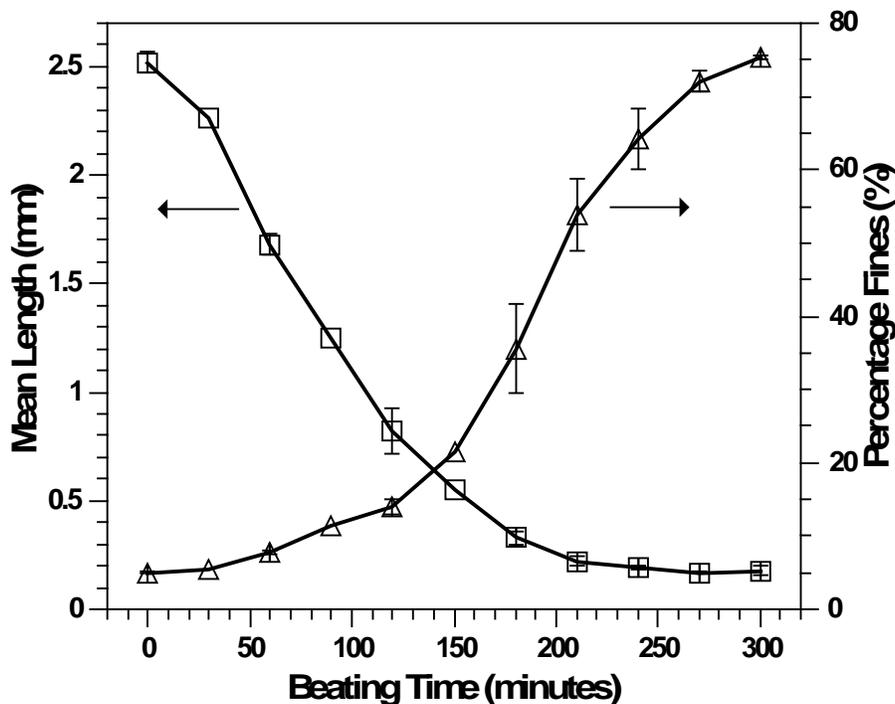
Fig. 1. Change in mean length and percentage fines (objects shorter than 200 micrometer) with the increased beating time. Duplicate experimental results are shown, indicating repeatability.

SEM images of freeze-dried and air-dried samples showed that the beating decreased the fiber size and liberated microfibrils. The images of the air-dried material in Fig. 2 show that the fibrous structure on the surface did not exist anymore for the sample after 5 hours of beating. The microfibrillated cellulose when dried formed a film without significant micro-pores (approximately not more than 1.1 micrometer of diameter for 180 minutes of beating time and no micro-pores in the film samples beyond 180 minutes of beating time), which is apparent at the lower magnification. These images were obtained from samples after the collapse of the fiber network during drying. In order to better distinguish the state of the fibers and microfibrils in the water suspension before drying, SEM images of freeze dried samples were taken, as shown in Fig. 3. It is clear that at the higher magnification, the bulk wall of the fiber changed from a solid mass to individual microfibrils. These microfibrils have diameters in nanometers and an accompanying large specific surface area (Spence *et al.* 2010, 2011).
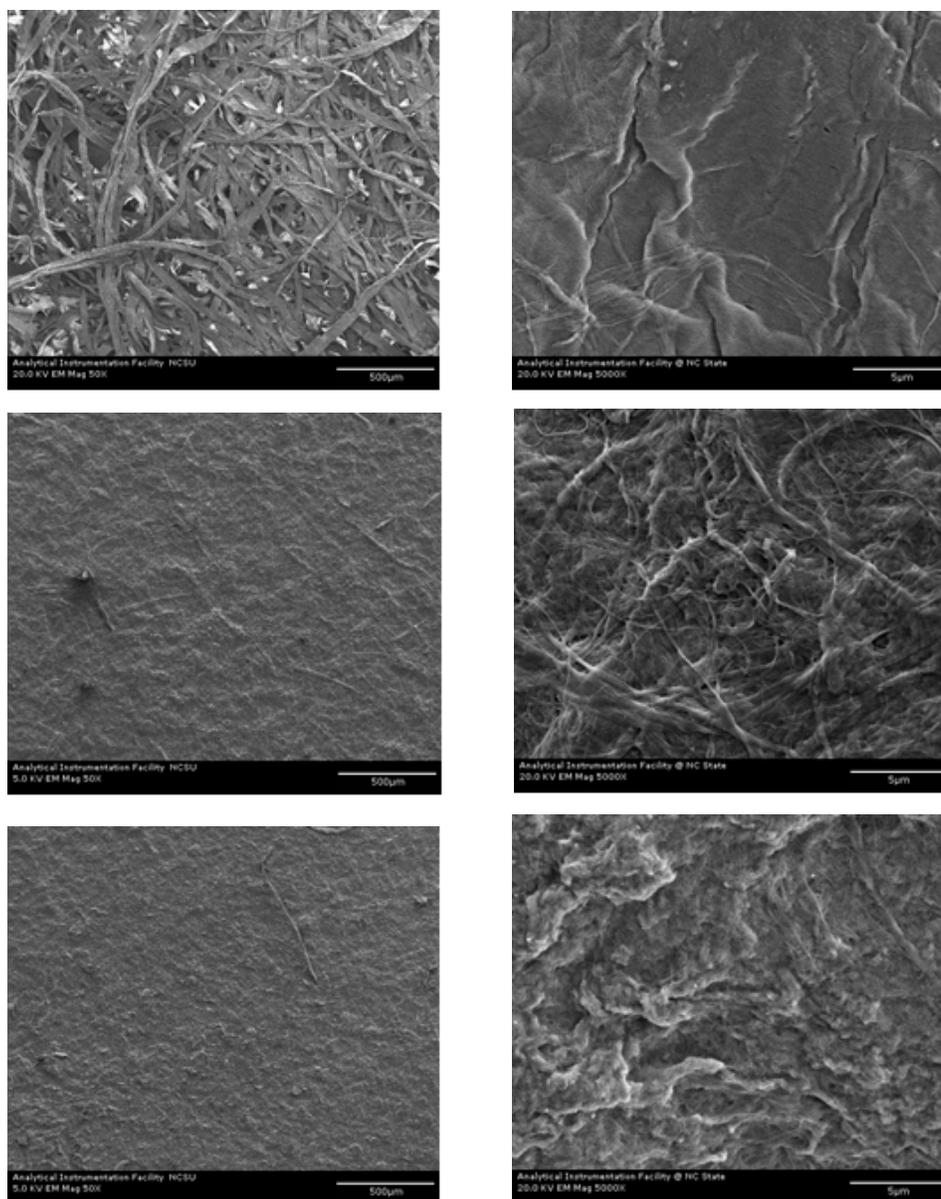
Fig. 2. Surface of air-dried sheet observed by SEM at constant humidity. Top to bottom are 0, 3, and 5 hours beating. Length scale on left of 500 microns and on right of 5 microns.

Drying Behavior of Fibers

In an earlier publication, in the case of fibrous surface (with pulps prepared with beating times of up to 40 minutes, Park *et al.* 2006a), drying kinetics using a TG furnace revealed three different drying regimes, which are a warm-up zone, a constant rate zone, and a falling rate zone, as most easily observed in the first derivative curve in Fig. 4. When a sample is initially placed in the TG furnace, the drying rate increases as the sample warms up, indicating a warm-up zone. The evaporation rate then remains relatively constant for a time. The existence of the constant rate zone over a wide range of time can be understood if the exposed surface is kept 'sufficiently wet' by the movement of moisture from the interior (Belhamri 2003; Schlünder 2004).
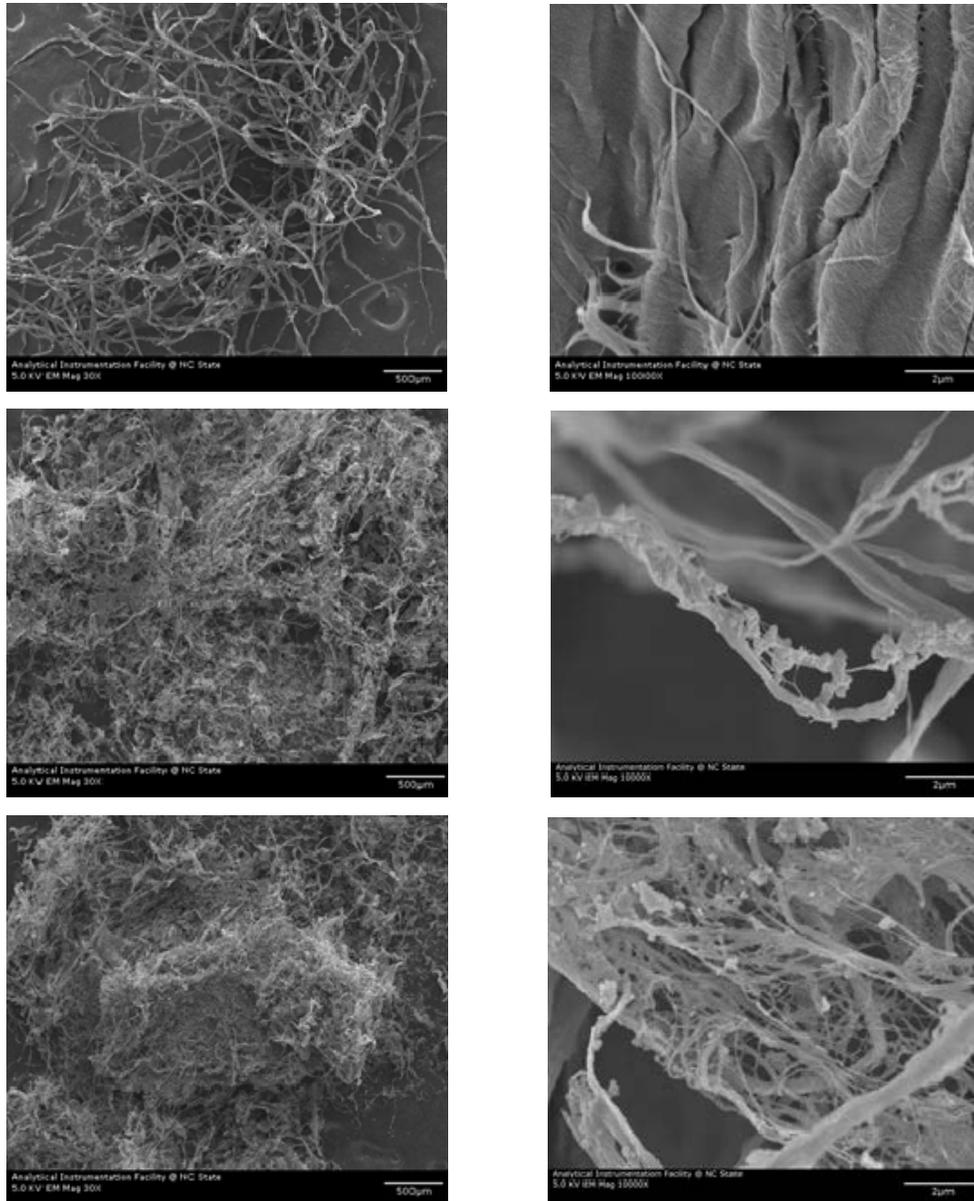
Fig. 3. SEM images of freeze dried samples collected at beating times from top to bottom of 0, 3, and 5 hours. Length scale on left of 500 microns and on right of 2 microns.

Schlünder showed mathematically that the condition for a sufficiently wet surface is fulfilled if the pore diameter of the porous material is small compared to the thickness of the viscous sub-layer formed by the gas flow past the surface and the pores are evenly distributed (Schlünder 1988).

The decrease in the drying rate in the falling rate zone can be attributed to a change in the mechanism of drying. When the movement of water is not sufficient to replenish the free water at the surface, the rate of drying falls. The rate of drying thus is governed by the internal diffusion, which is dependent on properties such as fiber/microfibril type, pore volume and geometry, fiber wall thickness, and moisture ratio. Thus, the constant rate zone is indicative of large volumes of external water to the fiber cell wall, which can evaporate freely.
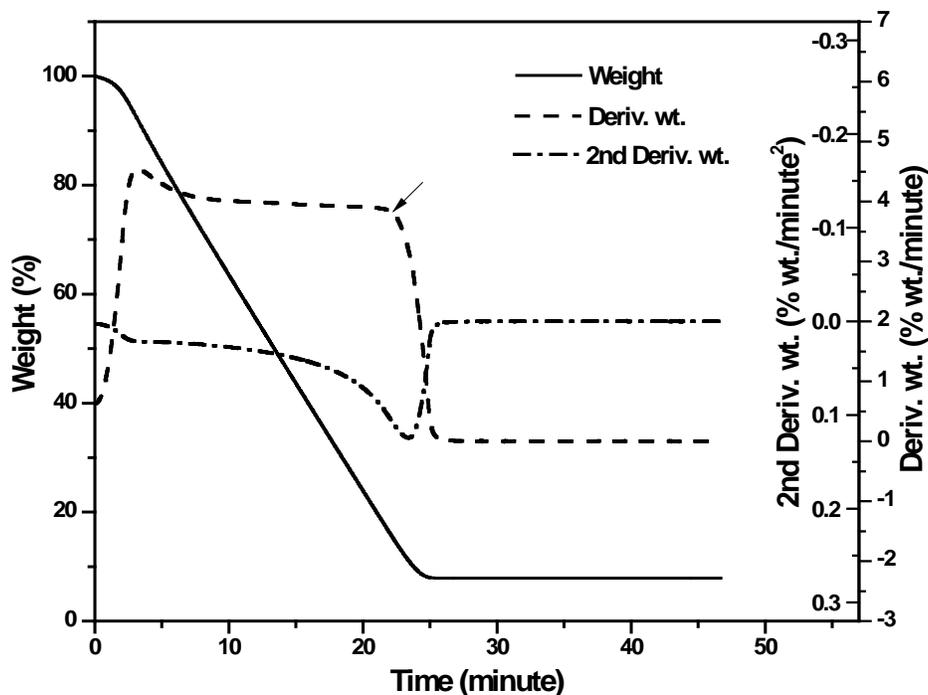
Fig. 4. TGA analysis of an unbeaten bleached softwood pulp sample at an isothermal temperature of 90 °C. The filled arrowhead (at 22.25 minutes) indicates the critical point, representing the end of the constant rate drying zone and the beginning of the falling rate zone.

The hard-to-remove water is the water remaining in the pores and capillaries of the fiber wall, which are removed at a slower rate after the bulk water evaporates. This slower rate of drying is presumably associated with the smaller features (cracks, pores, voids between fibrils, fibril intersections) of the material (Park *et al.* 2006b). In this regime, as the water is progressively removed from the pores of the solid, the fraction of pore volume that is occupied by air increases. When the fraction reaches a certain limit, there is insufficient water left to maintain continuous films across the pores and the pores fill with air, which now becomes the continuous phase.

According to the definition, 'hard-to-remove water' (in Park *et al.* 2006a) is the moisture ratio of fibers at the transition between the constant rate zone and the falling rate zone during the isothermal drying of fibers and fiber suspensions containing microfibrils. The transition zone was defined as the time at which twice the average value of the 2nd derivative in the constant rate zone was reached. The issue with this definition occurs when a pronounced constant rate zone is not apparent. In this case, ambiguity in the transition zone determination is realized. The complete drying is defined as the point at which the derivative of the weight loss reaches 0.001 %/min. The amount of water at the transition point divided by the final solids provides the HR-water content in grams of water per gram of solids.

Drying Behavior of Fibers and Microfibrils

As beating time increases, however, fibers are converted into microfibrils and both exist in the material. Figure 5 shows the drying behavior of the predominantly microfibrillated cellulose generated after five hours of beating. It is observed that a constant rate drying zone does not appreciably exist in these kinds of samples. A second

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critical moisture content is observed in the falling rate zone. This can be identified as a local minimum in the 2nd derivative curve, approximately 18 minutes in Fig. 5, indicated with an unfilled arrowhead. The standard deviation of the first and second critical times have been calculated from independent sets of experiments and were found to be about 1-2%. The trend of these two critical times decreasing with increasing beating of fibers was reproducible.

This second critical point in drying has not been reported previously. By inspection of the weight loss versus time data in Fig. 5, it is reasonable to expect that most water-sample interaction measurement methods performed isothermally utilizing the weight (or other variable) versus time (not the first derivative or second derivative) would simply not reveal a second critical point.

For these types of samples with microfibrils, the HR definition as described above is very difficult to apply. A new measure that reflects the hard-to-remove-water is introduced in this study which can be effective for both fibers and microfibrils. This method is not supposed to physically reflect the quantitative amount of water, but simply be used to reflect the amount of water-fiber interaction. It is defined as the area above the drying rate curve after the heat up zone, as can be seen in Fig. 6. Point S is defined as the point where the drying rate is maximum, and point F is the point where the second derivative is minimum nearing the completion of the weight loss process. The area SGFS represents the area above the first derivative curve. This definition does not require a pronounced constant rate drying zone for application. The weakness of this method is that it does not indicate a quantitative amount of water.
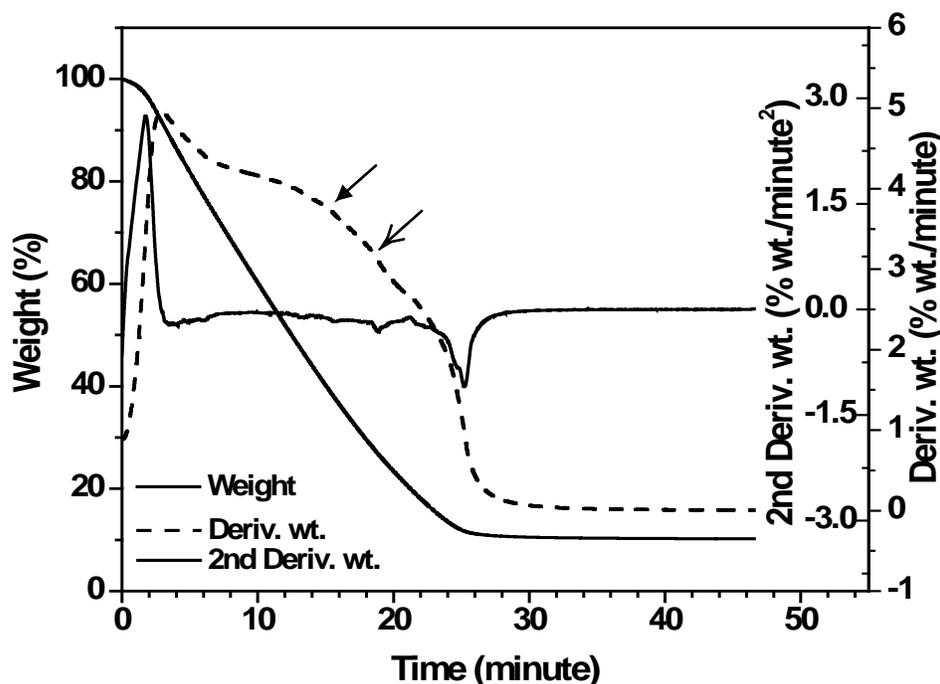
Fig. 5. TGA analysis at an isothermal temp of 90 °C for sample with 5 hours beating time. A first critical point is indicated with the filled arrowhead and the second critical drying point is indicated with an unfilled arrowhead.

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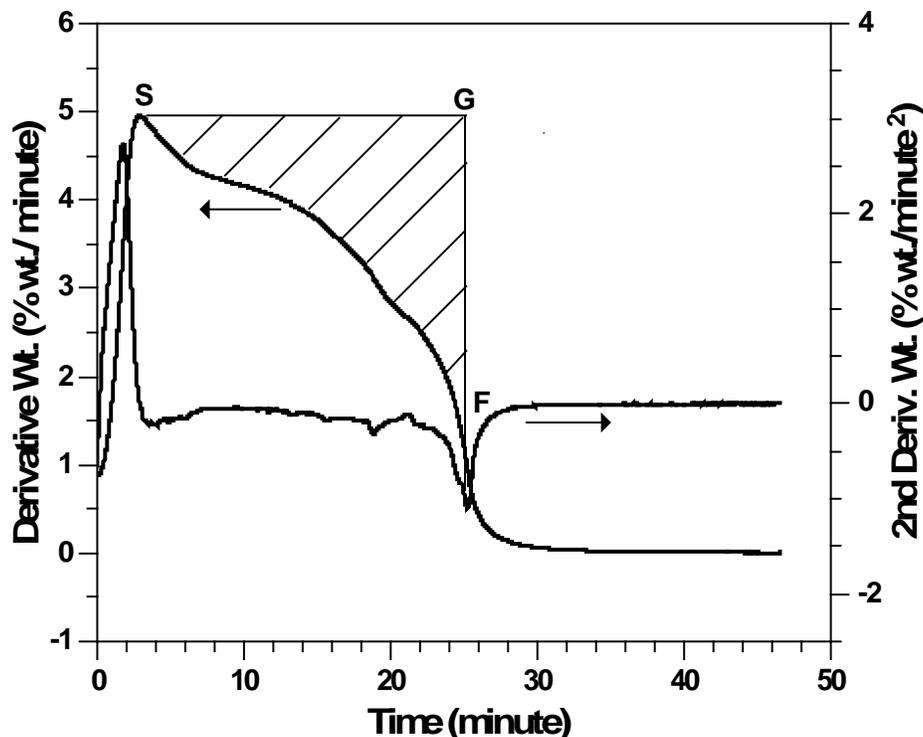
Fig. 6. HR water content determined by the area defined in this study

The weight loss versus time, the first derivative of weight loss, and second derivative of weight loss are shown in Fig. 7. It can be noticed from careful inspection of Fig. 7a that the highly beaten samples dry slower and continue to lose small amounts of mass even after 40 minutes of drying, which is not apparent in the unbeaten fibers. When the first and second derivatives are inspected, other interesting differences are revealed, the main difference being in the decreased constant rate drying zone time with increased beating. In the case of no beating (0 minutes) in Fig. 7b, the area above the curve will be small due to a prominent constant rate zone. The area above the first derivative of weight loss data has a significant contribution from the falling rate zone. As beating time increases, the constant rate zone starts to diminish and for fibers with low or no constant rate zone in Fig. 7b (120 to 300 minutes), and the area above the curve will be greater.

The second critical point is indicated on Figs. 7b and 7c with unfilled arrowheads for the 180, 240, and 300 minute samples at 23.1, 22.1, and 18.7 minutes, respectively. This second critical point may be due to another complication occurring during drying which is pore/void closure (Park *et al*. 2006b). If all the voids between the solid elements are closed in the matrix due to drying contraction, then the moisture will have to diffuse throughout the cellulose bulk structure to be removed, which is presumed to be a very slow process. For example, Fig. 2 shows a much tighter void structure with dense packing for the 5 hours beaten material relative to the 0 hour beaten material (low magnification). For the 5 hours beaten material, the path that water must take includes significant diffusion through the bulk material that does not contain macro-voids. Significantly longer diffusion lengths are required in this case. It is suggested here that the second critical point observed with the microfibril element containing materials is due to the continuous, macro-void free structure developed in the material. Certainly more research must be performed to understand the origin of this second critical point.
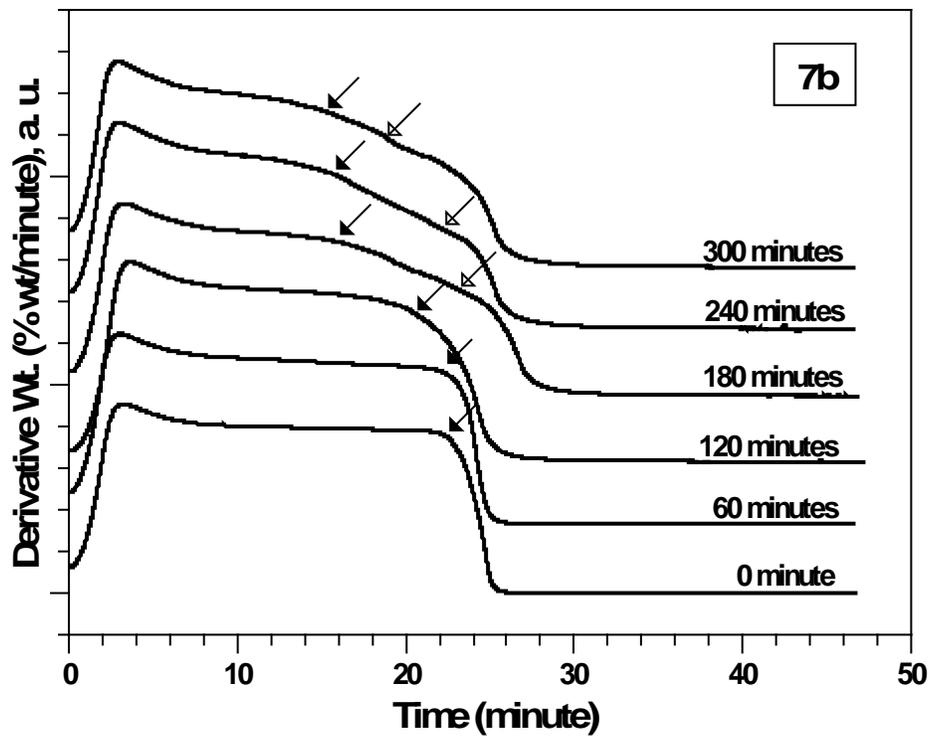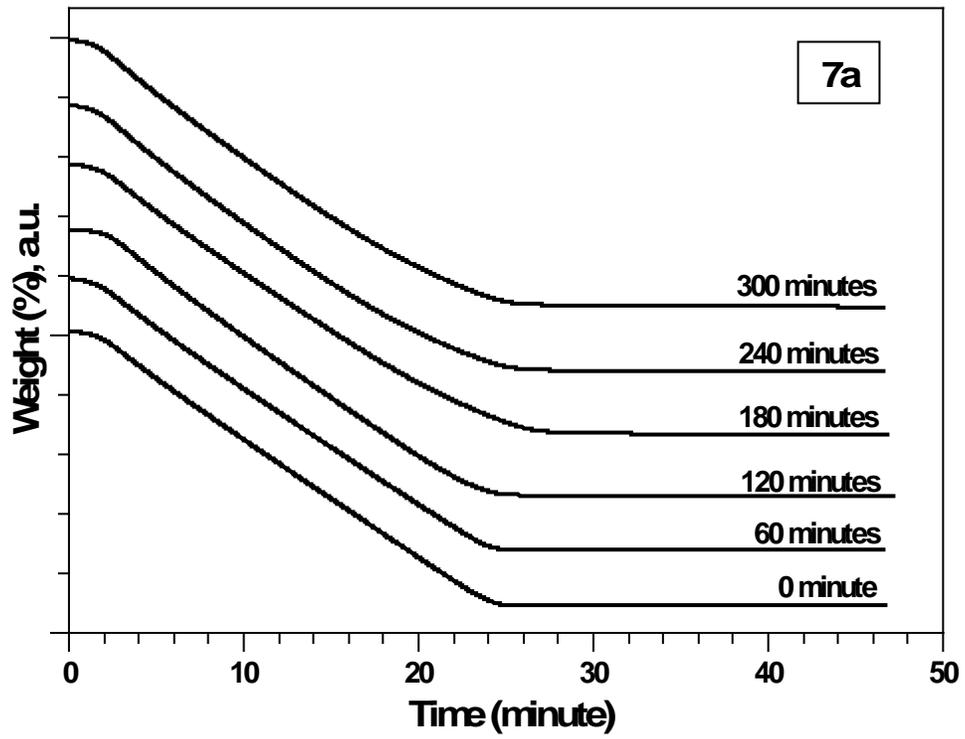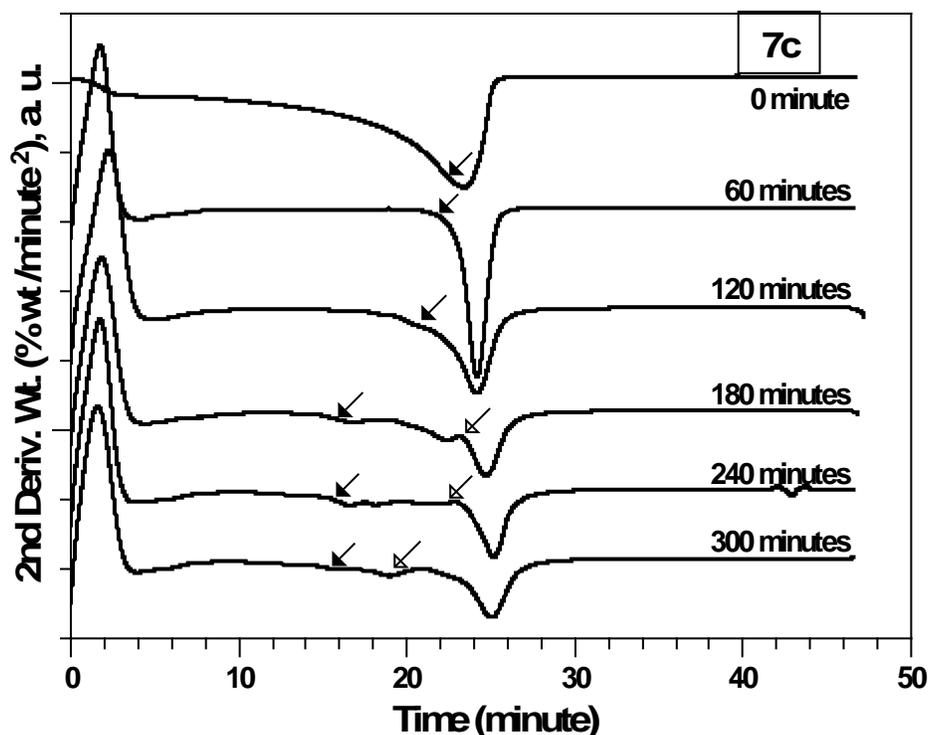
Fig. 7. Comparison of drying rate at isothermal temperature of 90 °C with beating time, (a) weight loss versus temperature, (b) derivative weight loss versus temperature, and (c) 2nd derivative weight loss versus temperature. First critical point is indicated with the filled arrowhead and the second critical drying point is indicated with an unfilled arrowhead. The x-axis range spans 9% wt/min; however, individual curves have been stacked by arbitrary levels.

Comparison of the Two Methods to Characterize Water Interactions

Both methods to characterize the amount of sample-water interaction, (1) by identifying the first critical point and calculating the HR water (Park *et al.* 2006a) and (2) by integration of the area above the 1st derivative curve, were performed on all of the samples, and the results shown in Figs. 8 and 9 versus beating time, respectively. A reasonably linear correlation between the two methods exists at low beating times, as shown in Fig. 10, but with longer beating times the scatter in the data becomes more pronounced. This study indicates that both methods can be used as a gauge for water-sample interactions.

It was also of interest to determine if higher water-sample interactions correlated with a total drying time increase. Figure 11 indeed shows that the drying time, as defined as the time in which a weight loss rate of 0.001%/minute is realized, increased with beating time, another indication of water-sample interactions. However, the increase in time was only about 15%, and the correlation strength was weaker, as indicated by the low R^2 value.

Also of interest was the moisture ratio at the second critical point versus beating time, Fig. 12. The second critical point was observed for pulps with beating times of 3 hours or greater, see Fig. 7. Figure 12 shows the average of two points for each beating time. Both the moisture ratio for the first and second critical points increase with beating, with some scatter, with the first critical point being more sensitive (higher slope) to beating time than the second critical point.
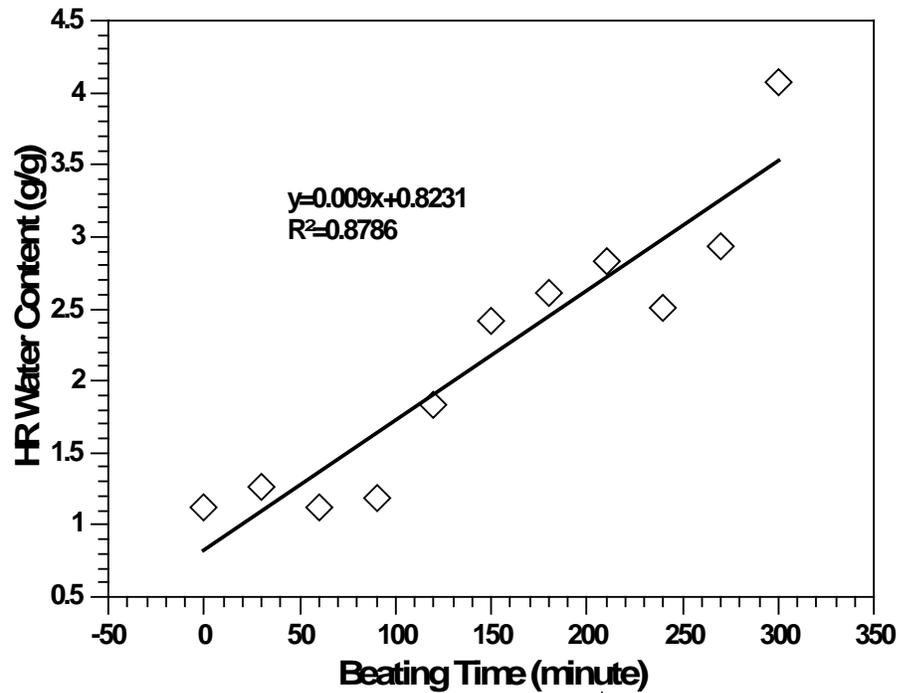
Fig. 8. HR water content calculated via the identification of the 1st critical point method versus beating time
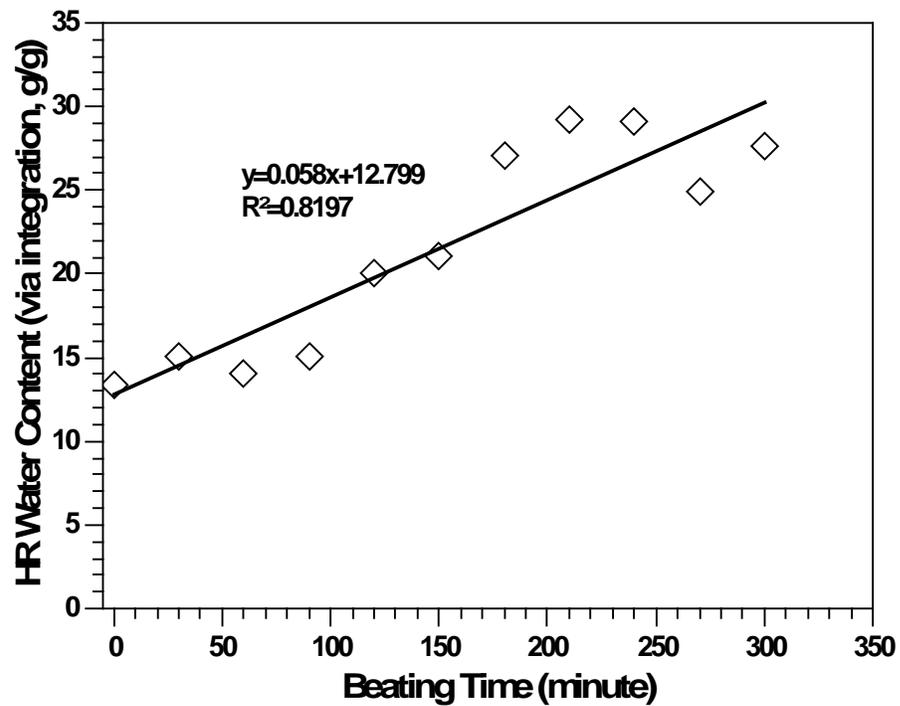
Fig. 9. HR water content calculated via 'integration' method defined in this study versus beating time
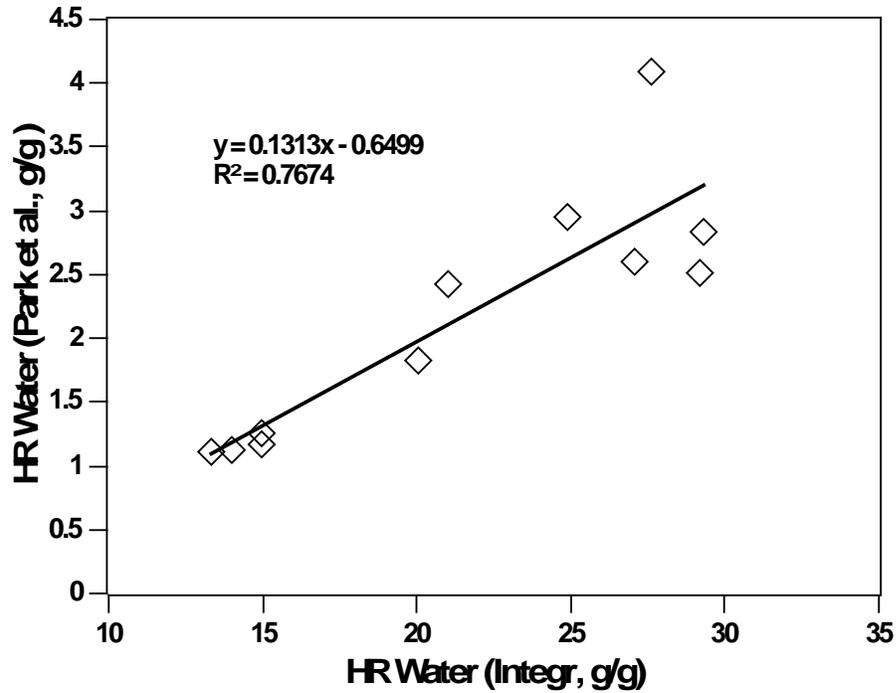
Fig. 10. Comparison of HR water content calculated via integration and via critical point methods. This figure shows that initially when fibers are in excess then both can be correlated, but when microfibrils are in excess, the correlation is weaker.
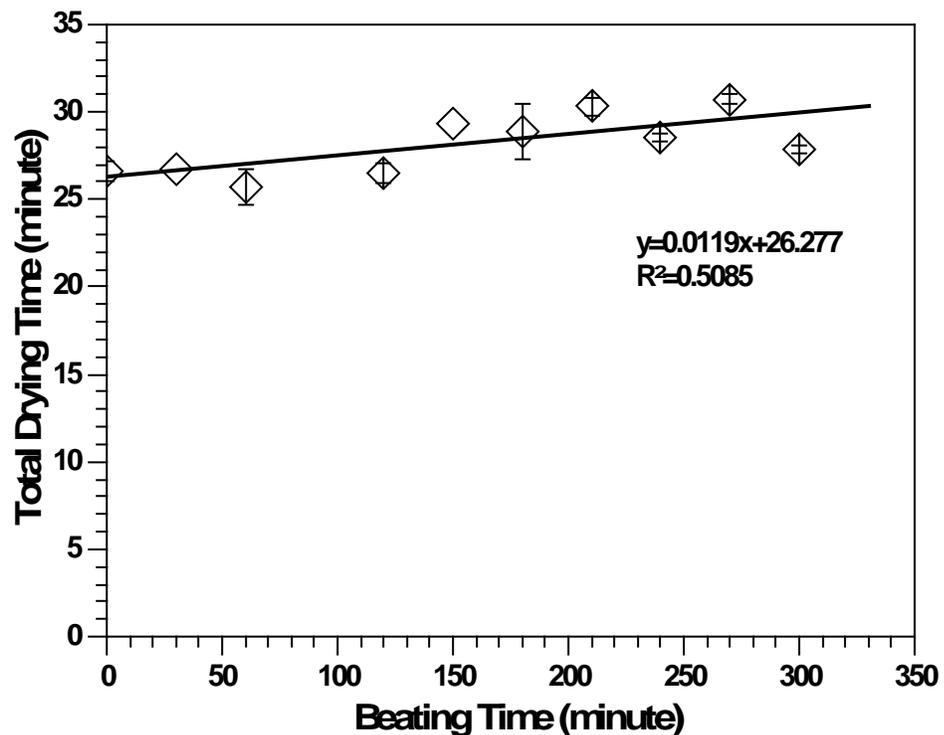
Fig. 11. Effect of beating on the total drying time of samples
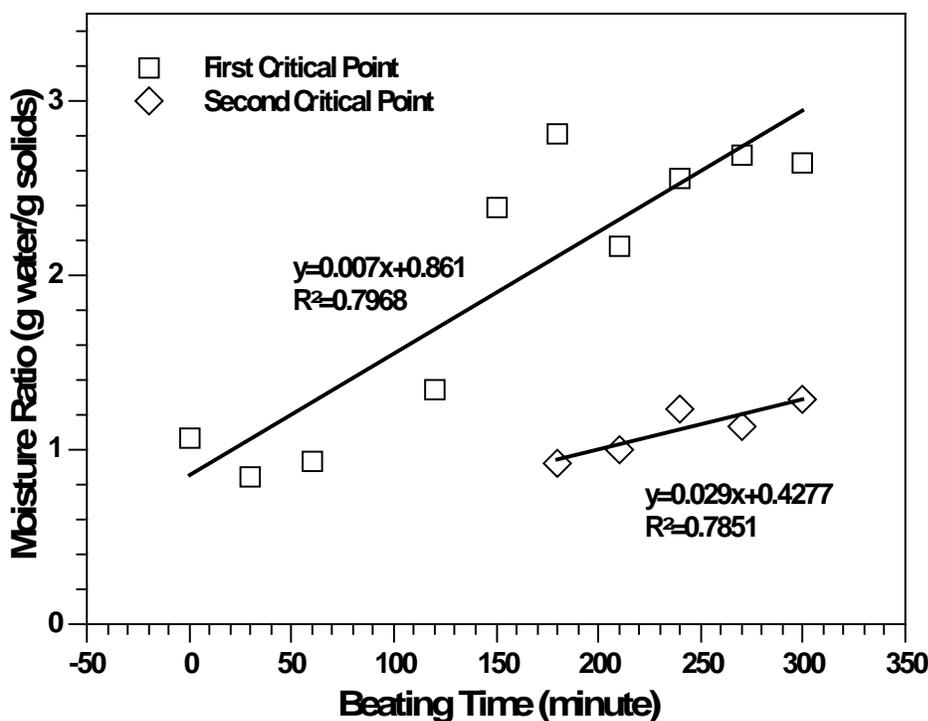
Fig. 12. Moisture ratio at the first critical point and second critical point versus beating time

In summary, it has been observed that with increasing beating time, the fiber length decreases, and after beating for more than 210 minutes, the average fiber length is lowered to 200 micron (Fig. 1). The SEM images (Fig. 2) of the air dried film surface showed that with increasing beating time, the pores initially present in the case of non-beaten fibers are diminished and the film prepared from the fibers after 5 hours of beating time revealed no micro-pores. From Fig. 7b it is clear that with an increase in beating time the constant drying rate zone started to diminish, and after 5 hours of beating, the constant drying rate zone was essentially non-existent. This, in turn, signifies that as the beating time increases, the easy to evaporate water content (external water to the fiber cell wall) decreases and the hard-to-remove water content (present in the pores and capillaries of fiber wall) increases. Figures 9 and 11 represent how the increasing beating time increased the hard-to-remove water content and total drying time, respectively. These results suggest that longer drying times or more drying energy would be required for drying microfibrillated materials relative to fibers.

Fiber Properties for Blends

The drying rates of three blended samples (80/20, 50/50, and 20/80 fiber/micro-fibrils) are shown in Fig. 13a (1st derivative of weight %) and Fig. 13b (2nd derivative of weight %). The first critical points are shown with filled arrow heads. The first critical points for three blends *e.g.*, 80 (0 hours)/ 20 (5 hours), 50 (0 hours)/ 50 (5 hours), and 20 (0 hours)/ 80 (5 hours) are identified at 20.8, 20.7, and 14.9 minutes, respectively. A constant rate drying zone was apparent for blends containing up to 50% of 5 hour beaten fiber. At the 20/80 fiber/ microfibril level the 2nd critical point was observed at 19.0 minutes, indicated as an unfilled arrow head.

SEM surface images of the air-dried sheet and freeze dried samples from 50/50 blends are shown in Figures 14 and 15, respectively. As expected, these SEM images show the presence of both the fiber and microfibrils in the 50/50 blend sample. Also note that for the air-dried sample, the surface is void-free, with a continuous film of microfibrils. Thus, the 50/50 blend sample appears to have similar surface characteristics to the void-free sample (beaten for 5 hours) having 100% microfibrils in Fig. 2 and does not have surface pores and features like the unbeaten fibers in Fig. 2. This indicates that the blends of fibers and microfibrils might have unique composite properties, enjoying surface properties developed by the microfibrils and bulk properties retaining some of the fiber properties such as tear strength. This is an important area for further research.
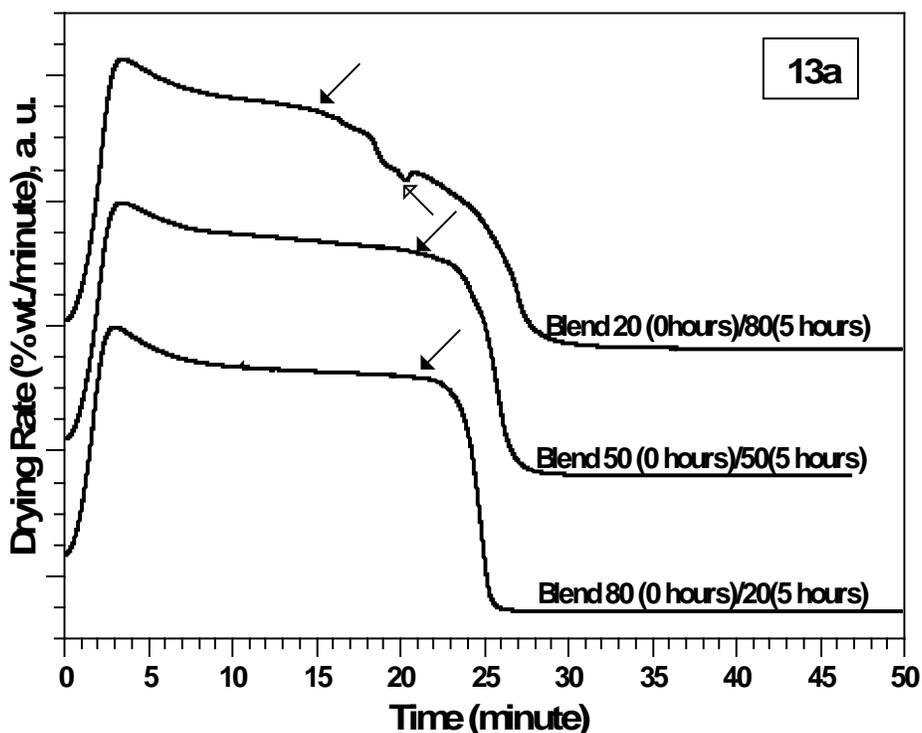
Fig. 13. Comparison of drying rate at isothermal temperature of 90 °C for the blends, (a) 1st derivative weight and (b) 2nd derivative weight. First critical point is indicated with the filled arrowhead, and the second critical drying point is indicated with an unfilled arrowhead.
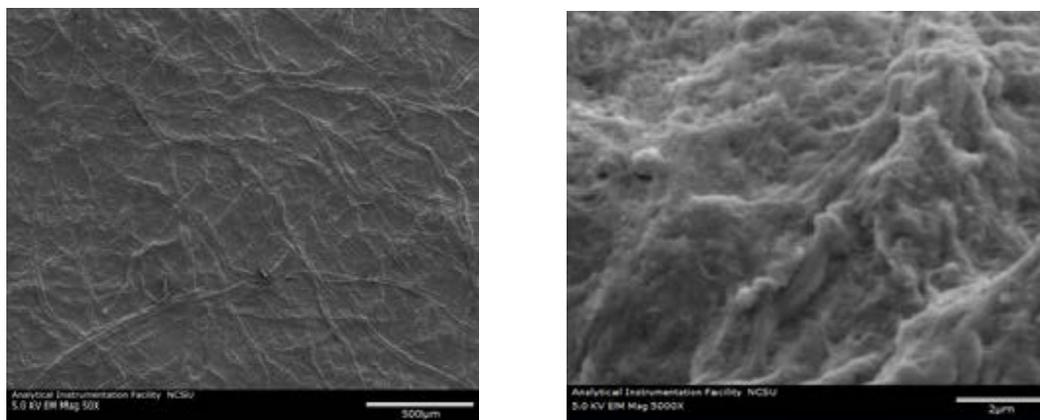
Fig. 14. SEM surface images for air-dried sheet from 50/50 blend at constant humidity. Length scale on left image is of 500 microns and on right image is of 2 microns.
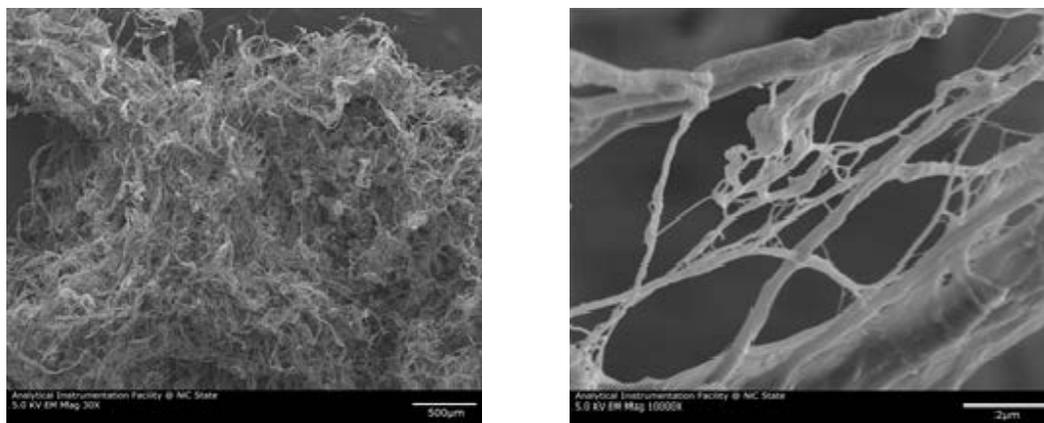
Fig. 15. SEM images of freeze dried blended samples of 50/50 blend. Length scale on left image is of 500 microns and on right image is of 2 microns.

CONCLUSIONS

1. Isothermal thermogravimetric analysis has been shown to be a convenient and insightful characterization method for fiber-water as well as microfibrils-water systems and allows a direct comparison of fibers and fibrils at a small sample size, *e.g.* 10 mg of dried mass.

2. SEM images showed that a prolonged beating converts the solid bulk wall of the large fibers to liberate microfibrils with diameters in nanometers.

3. When the microfibrillated cellulose materials are dried from water, a continuous film without macro-pores is formed. Materials with this structure have a diminished constant drying rate zone.

4. The microfibrillated cellulose materials take a longer time to dry than unbeaten fibers under the same drying conditions. This suggests that the net drying energy to prepare microfibrillated materials would be greater than that for unbeaten or moderately beaten fibers.

5. A new drying critical point was identified for microfibril-containing structures, hereby designated as a second critical moisture content in the falling rate zone. This can be observed as a local minimum in the 2nd derivative curve.

6. A new method to quantify the HR water content in both fibers and microfibrillated cellulose material is proposed based on the area above the first derivative curve, and this method for characterizing HR water is reasonably linear with the previous HR water calculation method.

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