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Surface modification of cellulosic fibers using dielectric-barrier discharge

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Abstract

The relationship between the surface chemistry of cellulosic fibers treated with an atmospheric cold plasma generated by dielectric-barrier discharge and recently discovered improvements in wet-strength and wet-stiffness was evaluated. ESCA characterization of cellulosic fibers indicates that treated fiber surfaces undergo selective oxidation, degradation, and removal of extractives and other contaminants. Fiber wettability in water increases with low dielectric-barrier discharge treatment (1.0 kW m^{-2} min), but diminishes with increased treatment intensity (5.0 kW m^{-2} min). This is related to changes in the polar and dispersive components of surface energy as determined by dynamic contact angle analysis. ESCA, combined with analysis of wettability and wet-strength properties, reveals that reductions in surface energy at increased treatment levels occur due to oxidative reactions.

Keywords: Cellulose; Kraft pulp; ESCA; Dynamic contact angle; Surface energy; Plasma; Oxidation; Dielectric-barrier discharge; DBD

1. Introduction

The need for innovative green chemistry processes and societal demands for the development of sustainable manufacturing procedures has led to a renaissance in cellulosic chemistry (Mullholand, Sylvester, & Dyer, 2000). Along with conventional applications for cellulosic fibers, a host of new applications are being rapidly pursued. As reviewed by Cavaille (1995) and Gatenholm, Felix, Kalson, and Kubat (1992), the reinforcement of plastics with cellulosic fibers provides the opportunity to improve physical properties and reduce the amounts of petroleum-based hydrocarbons required for assorted products. These concepts have been further refined with the development of novel cellulose biocomposites in which all components are derived from renewable resources (Mohanty, Misra, & Hinrichsen, 2000; Toriz, Arvidsson, Westin, & Gatenholm, 2003). In these applications and with conventional cellulosic materials, the surface chemistry of cellulosic fibers plays a pivotal role in the overall physical properties (Koljonen, Österberg, Kleen, Fuhrmann, & Stenius, 2004; Trejo-O'Reilly, Cavaille, & Gandini, 1997). Studies by Carlsson, Gilbert, Eriksson, and Lindstroem (1994) and Carlsson, Stroem, and Annergren (1995) have shown that low-pressure cold plasma of O, N, Ar, or air can be employed to improve the water sorption of chemical and mechanical pulps. The authors further demonstrated the ability of utilizing ESCA and fiber wettability measurements to investigate the improvements in the water absorption of pulps. Although a variety of methods have been developed for modifying the surface chemistry of cellulosic fibers, one of the most promising is the use of an atmospheric cold plasma generated by dielectric-barrier discharge; especially in light of its versatility and potential practical applications (Kogelschatz, 2003; Rehn & Viöl, 2003; Vander Wielen & Ragauskas, 2004a, 2004b).

The use of non-thermal plasma treatment of polymer surfaces to promote wettability, printability and adhesion has also been reported in the literature (Uehara, 1999). At atmospheric pressure, essentially there are two methods for producing non-thermal plasma using either a corona discharge or a dielectric-barrier discharge. Corona discharges are due to inhomogeneous electrode geometries such as a point electrode and a plane. The discharge takes place near sharp points where the electric field is enhanced. A way to avoid formation of sparks and essential current growth in the channels formed by streamers is to place a dielectric barrier in the discharge gap (Roth, 2001). Obviously, the presence of a dielectric barrier in the discharge gap precludes DC-operation of DBD, which

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usually operates at frequencies between 0.5 and 500 kHz. Sometimes, the dielectric-barrier discharges are also called silent discharges, because the absence of sparks makes these discharges silent. An important advantage of the dielectric-barrier discharge is the simplicity of its operation in strongly non-equilibrium conditions at atmospheric pressure and at reasonably high power levels, without using sophisticated pulse power supplies. The dielectric-barrier discharge proceeds in most gases through a large number of independent current filaments usually referred to as the micro-discharges. These micro-discharges, from a physical point of view, are actually streamers that repeatedly strike at the same place as the polarity of the applied voltage changes, thus appearing to the eye as bright filaments. Micro-discharges are self-organized taking into account charge accumulation in the channel volume and on the dielectric surface. The short duration of current leads to low overheating of the streamer channel, and the DBD plasma remains strongly non-thermal. The plasma generated by dielectric-barrier discharge in ambient air is known to generate a host of reactive oxidative intermediates including OH, N, O, O_3, exited states of N_2 and O_2 and atomic oxygen and nitrogen (Kogelschatz, 2003; Naidis, 1997). These species are generated by electron collisions in the discharge and initiate different reaction paths leading to production of reactive intermediates. These reactive intermediates provide a convenient resource for surface activation of polymeric materials including cellulosics.

Recently, Vander Wielen, Page, and Ragauskas (2005) and Vander Wielen and Ragauskas (2004b) have explored the use of atmospheric dielectric-barrier discharge to enhance the physical strength properties of bleached kraft pulps. Serendipitously they discovered that atmospheric dielectric-barrier discharge could be employed to improve the wet-strength and wet-stiffness of paper prepared from chemical pulps. Indeed, these recent findings demonstrate that the wet-strength of bleached kraft paper could be enhanced by 50–70% by treatment with dielectric-barrier discharge generated cold plasma. Although prior studies have highlighted the link between increased surface oxidation and hydrophilicity with plasma treatment, no definitive studies have examined the relationship to wet-strength properties and the atmospheric cold plasma oxidation of cellulosic fibers (Back & Danielsson, 1987; Brown & Swanson, 1971; Goring, 1967).

The use of ESCA to analyze the surface of cellulosic fibers is a frequently employed technique that can detect changes in the surface components of cellulosic wood-derived fibers including the presence of surface lignin, extractives and carbohydrates (Börås & Gatenholm, 1999a; Gray, 1978; Henriksson & Gatenholm, 2001; Johansson, Campbell, Koljonen, & Stenius, 1999; Koljonen, Österberg, Johansson, & Stenius, 2003). Of special significance to this study is the ability of ESCA to differentiate between differing oxidation states of carbon on the surface of cellulosic fibers.

An alternative method of evaluating changes in the surface chemistry of cellulosic fibers can be accomplished indirectly via dynamic contact angle analysis using the Wilhelmy plate technique (Miller, Penn, & Hedvat, 1983). This technique has been employed to investigate changes in the surface of celluosic fibers that were modified with succinic anhydride (Gellerstedt & Gatenholm, 1999) and styrene (Young, 1976). Dynamic contact angle (DCA) analysis by the Wilhelmy plate method, in comparison with the sessile drop method, is less affected by the absorbency or surface roughness of the fiber mat. DCA analysis provides information regarding the dispersive and non-dispersive components of fiber surfaces using probes with known polar and dispersive characteristics. The purpose of our study was to apply these complementary techniques to characterize changes to cellulose fiber surfaces at relatively low and high dielectric-barrier discharge treatment intensities so as to determine the fundamental mechanisms involved in the recently reported cold plasma enhancement of wet-strength/stiffness of kraft pulps.

2. Experimental

2.1. Materials

Methylene iodide was purchased from Sigma and acetone was acquired from VWR. The starting pulp used for this study was the long fiber fraction isolated from a commercially manufactured elemental chlorine-free fully bleached softwood chemical wood pulp, using a Bauer–McNett fractionator to separate the fibers by screening according to standard TAPPI test method T-233 (Tappi Test Methods, 2002/2003). Pulp fibers were shown to contain 0.85% lignin and an extractives content of 0.037%, as determined by standard TAPPI test methods. The fibers were formed into test sheets as previously described (Vander Wielen & Ragauskas, 2004a, 2004b), then restraint dried in brass rings at 50% relative humidity. A portion of the plasma treated and reference sheets were acetone-extracted with a Soxhlet apparatus for 24 h prior to surface analysis.

2.2. Physical properties

Both the wet-tensile and wet-stiffness index for samples of reference and treated cellulosic fibers were tested using a Model 1122 Instron tensile testing apparatus with a 2.00 kg load cell. A variation of Tappi test method T-494, in which samples were soaked in nano-pure water for 5.0 min prior to analysis, was used (Tappi Test Methods, 2002/2003).

2.3. Surface modification

A Sherman Treater laboratory station equipped with a GX10 power generator and a stationary ceramic-coated aluminum treatment electrode were used to apply a cold plasma to sheets attached to the moving aluminum ground electrode at controlled velocities. Treatment intensities of 1.0 and 5.0 kW m^{-2} min were applied to test sheets at atmospheric temperature (23.5 °C) and pressure.

2.4. Characterization of surface energy

The Wilhelmy plate technique was applied to determine the wettability of treated and untreated fibers utilizing a CAHN

Instruments, Inc. DCA-332 at a stage speed of 20 μm s^{-1} (Gellerstedt & Gatenholm, 1999). Ten single fibers were randomly selected from the acetone-extracted reference and treated paper sheets. These fibers were mounted to an adhesive tape and attached to a microbalance. The average advancing contact angles of methylene iodide (surface tension of 50.8 mN m^{-1}) and distilled water purified in a Millipore water purification system (surface tension of 72.8 mN m^{-1}) were determined. The average advancing contact angles in each test liquid, resulting from 10 individual fibers per treatment condition, were averaged and used to calculate the polar and dispersive contributions to surface energy using the harmonic mean method.

2.5. ESCA analysis

A Quantum 2000 Scanning ESCA Microprobe from Physical Electronics (Physical Electronics, Chanhassen MN, USA) equipped with a charge neutralizer, located at Chalmers University of Technology, was employed to characterize the effect of dielectric-barrier discharge treatment on the surface chemistry of (1) reference and treated samples that had not been further processed, and (2) that had been acetone-extracted. The samples were mounted and placed in a 10^{-8} Pa vacuum chamber where a monochromatic Al Kα X-ray source of 20.8 W, with a 100 μm beam size, and a 45° take-off angle was used to analyze 500 μm × 500 μm samples (Oestenson & Gatenholm, 2005). The survey spectra were performed from 0 to 1100 eV binding energy and Multipak software from Physical Electronics was used for deconvoluting C(1s) peaks and determining peak intensities.

3. Results and discussion

The surface modification of test sheets was accomplished employing a dielectric-barrier discharge method previously described in the literature (Vander Wielen & Ragauskas, 2004a, 2004b). Representative treatment levels and resulting changes in wet-strength properties are summarized in Table 1 for comparison with the surface analysis data. The wet-tensile and wet-stiffness of the paper increased with extended dielectric-barrier discharge treatment.

As previously demonstrated in the literature, the use of ESCA and surface energy measurements provides a unique insight into the surface oxidation chemistry initiated by a cold plasma treatment. To determine how surface properties vary with the changes in wet-stiffness and wet-strength upon dielectric-barrier treatment we utilized these techniques to gain insight into fundamental mechanism(s) contributing to these effects.

Table 1
Dielectric-barrier discharge treatment conditions and resulting changes in physical properties of cellulosic test sheets

Sample	Dielectric-barrier discharge (kW m^{-2} min)	Wet-tensile index (N mg^{-1})	Wet-stiffness index (N mg^{-1})
Reference	0	0.53	45.5
Low treatment	1.0	0.57	48.1
High treatment	5.0	0.63	67.5

3.1. Surface energy

Cellulosic kraft fibers were treated at various dielectric-barrier discharge levels (0, 1.0 and 5.0 kW m^{-2} min), and acetone-extracted. They were then examined using the Wilhelmy plate technique (Gellerstedt & Gatenholm, 1999; Young, 1976). Tensiograms (Fig. 1a–c) indicated increased wetting at low plasma treatment (1.0 kW m^{-2} min) which diminished at high treatment (5.0 kW m^{-2} min). Along the length of the fiber, variation in the force measured may be attributed to changes in the fiber perimeter, surface roughness and the heterogeneity of the surface chemistry (Berg, 1989) with the advancing contact angle showing heightened sensitivity towards low surface energy materials and the receding contact angle showing more sensitivity towards high surface energy materials (Johnson & Dettre, 1964). By comparing the magnitude of variation in amplitude among advancing and receding contact angles, it appears that the

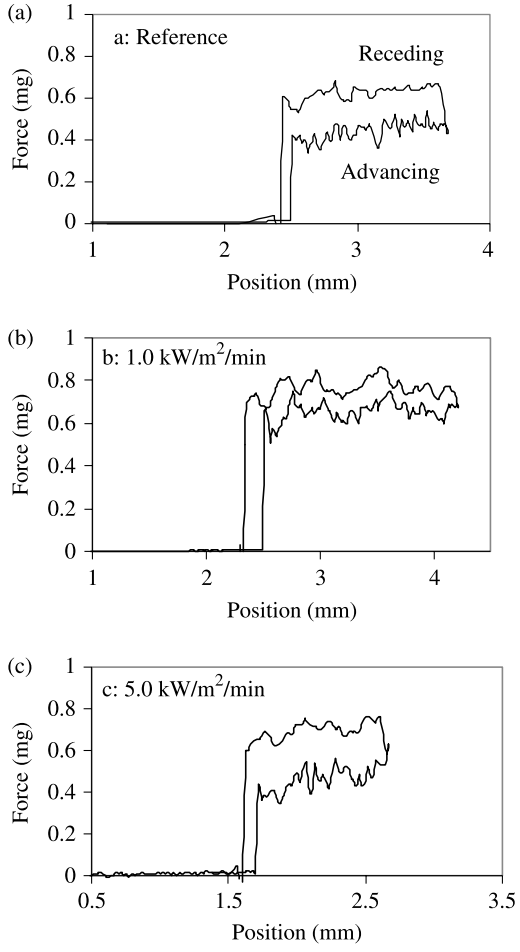

Fig. 1. Tensiograms from dynamic contact angle analysis of acetone-extracted cellulose fibers generated from (a) untreated samples, (b) samples treated at low cold plasma treatment intensity and (c) samples treated at high cold plasma treatment intensity.

Table 2
Advancing contact angle (θ_a) and dipersive (γ_d) and polar (γ_p) components of the surface energy (γ_{tot}) of acetone-extracted dielectric-barrier discharge-treated cellulosic fibers

Treatment (kW m^{-2} min)	θ_a in Water (°)	γ_{tot} (mJ m^{-2})	γ_p (mJ m^{-2})	γ_d (mJ m^{-2})
0	33.6	65.1	34.5	30.6
1.0	30.4	65.3	37.7	27.6
5.0	43.2	58.3	31.1	27.2

surface of the fibers treated at the lower dielectric-barrier discharge treatment intensity (Fig. 1b) shows the greatest variation in amplitude among receding contact angles. This data suggests increases in hydrophilic areas on fiber surfaces and/or increased surface roughness on the fibers upon cold plasma treatment (Fig. 1a–c).

The advancing contact angles of distilled water and methylene iodide on the fiber surface were measured and used to calculate the polar and dispersive contributions to surface energy by the harmonic mean method. This analysis

Table 3
Atomic composition and carbon C(1s) deconvolution peak intensities of untreated and dielectric-barrier discharge treated fibers characterized by ESCA

Plasma treatment (kW m^{-2} min)	Atomic composition			C1(s) deconvolution peak intensities			
	O(1s) (%)	C(1s) (%)	O/C ratio	C1 (%)	C2 (%)	C3 (%)	C4 (%)
0	43.70	56.30	0.78	13.8	63.3	19.4	3.5
1.0	45.71	54.09	0.84	8.9	70.2	17.4	3.5
5.0	45.81	54.09	0.84	5.8	64.9	24.1	5.2

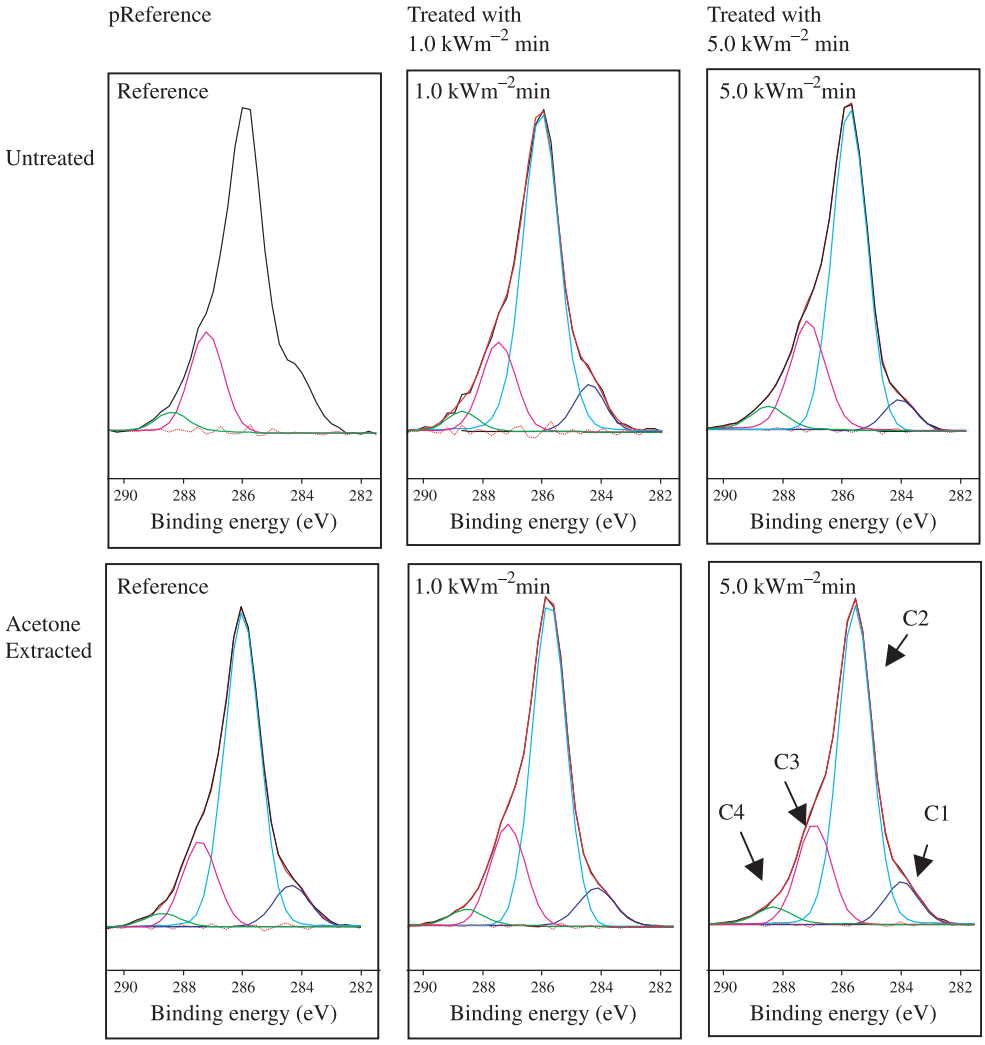

Fig. 2. ESCA deconvolution spectra for C(1s) signals for untreated and dielectric-barrier discharge treated, acetone-extracted untreated and dielectric-barrier discharge-treated cellulose fibers.

indicated diminished surface energy, and an increased advancing contact angle (θ_a) of water at the fiber surface at high (5.0 kW m^{-2} min) dielectric-barrier discharge treatment (Table 2). The polar component of surface energy (γ_p) was the largest contributor to this effect, and increased at the lower treatment level (1.0 kW m^{-2} min) along with a decrease in θ_a. These results, along with the tensiograms (Fig. 1), indicate an increased polar component surface energy and possibly surface roughness, along with a small increase in wettability, with low dielectric-barrier discharge treatment. This effect diminishes with increased dielectric-barrier discharge treatment intensity. The values summarized in Table 2 have standard deviations of four or less, and are similar to those seen for pulps in previous publications (Börås & Gatenhalm, 1999b).

3.2. Surface characterization

The surface chemical composition of untreated cellulose fibers and those modified by treatment with dielectric-barrier discharge at 1.0 and 5.0 kW m^{-2} min were characterized using ESCA. Fully bleached kraft fibers are expected to consist mainly of cellulose and some hemicellulose with only traces of residual lignin, extractives and other contaminants. Those used in this study contained 0.85% lignin and an extractives content of 0.037%, as determined by standard literature methods (Tappi Test Methods, 2002/2003) prior to acetone extraction. The theoretical O/C ratios for pure cellulose and hemicellulose are 0.83, and approximately 0.80, respectively. Lignin typically yields a value of 0.33–0.39 and extractives approximately 0.08 (Dorris & Gray, 1978a, 1978b). The ESCA O/C ratio of modified fibers was increased from 0.78 for untreated fibers up to 0.84 when dielectric-barrier discharge treated with 1.0 and 5.0 kW m^{-2} min treatment (Table 3). Since the O/C ratio of untreated fibers that had not been extracted was 0.78, the ESCA results for untreated cellulosic fibers suggest a trace presence of lignin and extractives on the surface of the fibers. As the O/C ratio increased to 0.84 with increased dielectric-barrier discharge treatment, oxidative reactions along with surface cleaning to remove contaminants, extractives and possibly lignin are indicated.

High-resolution deconvolution spectra for the C(1s) peak (Fig. 2) yields signals for C1 which represents carbon not bonded to oxygen, C2 represents carbon single-bonded to one oxygen atom, C3 represents carbon bonded to two single oxygen atoms or double-bonded to one oxygen, and C4 represents carbon single-bonded to one oxygen and double-bonded to another oxygen. The C1 deconvolution peak would not exist in pure, uncontaminated cellulose. However, bleached kraft fibers with small amounts of lignin, extractives, and other contaminants can contribute to this signal. The C1 deconvolution peaks and relative peak intensities for fibers that have not been extracted (Fig. 2) decline with increased dielectric-barrier discharge treatment (Table 4). This result suggests that the dielectric-barrier discharge treatment removes contaminants and extractives from the fiber surface. ESCA data analysis for the deconvoluted C2, C3, and C4 peaks for dielectric-barrier discharge-treated fibers indicates that treatment increases the occurrence of oxidized functionalities (Table 3).

Table 4
Atomic compositions of untreated and dielectric-barrier discharge-treated acetone-extracted fibers as characterized by ESCA

Plasma treatment (kW m^{-2} min)	Atomic composition		
	O(1s) (%)	C(1s) (%)	O/C ratio
0	44.55	55.45	0.80
1.0	44.48	55.52	0.80
5.0	43.96	56.04	0.78

Table 5
C(1s) deconvolution peak intensities of untreated and dielectric-barrier discharge-treated acetone-extracted fibers as characterized by ESCA

Plasma treatment (kW m^{-2} min)	C(1s) deconvolution peak intensities			
	C1 (%)	C2 (%)	C3 (%)	C4 (%)
0	9.15	69.90	18.02	2.94
1.0	9.22	66.22	20.96	3.60
5.0	8.66	66.57	20.83	3.95

Cellulosic fibers, treated by the same methods as previously described, were acetone-extracted prior to dielectric-barrier discharge treatment to remove contaminants and removable surface extractives. Once this occurred, no increases (Table 4) in the ESCA O/C ratios were observed supporting the prior suggestion that DBD treatment of unextracted fibers removes surface extractives and/or lignin.

Analysis of the ESCA C(1s) deconvolution peaks for acetone-extracted fibers (Table 5) indicates that the dielectric-barrier treatment increases the C3 and C4 peak amplitudes, while the C2 peak from carbon bearing hydroxyl groups decreases in intensity on prolonged treatment. This may indicate that upon dielectric-barrier discharge treatment oxidative reactions result in aldehyde/ketone and carboxylic acid group formation. In Espy's (1995) review of the mechanism by which additives improve wet-strength of cellulosic fibers, he proposed two general mechanisms: (1) a protective mechanism by which water is prevented from interrupting hydrogen bonding and (2) a covalent cross-linking mechanism. It is difficult to envisage the DBD treatment generating a protective coating about fiber cross-linking to enhance wet-strength. The data summarized in this study is supportive of a cross-linking mechanism whereby the newly formed oxidized cellulose structures could contribute to fiber cross-linking via an acetal or ester linkage. Indeed, the increased hydrophobic nature of the fibers as determined by contact angle measurements would be consistent with a cross-linking mechanism.

4. Conclusion

The wet-stiffening of bleached kraft fibers appears to be related to the degree of fiber modification, which is dependent upon dielectric-barrier discharge treatment intensity. The novelty herein lies in our examination of fundamental changes to the fiber surface. The decreased surface energy and

increased wet-tensile and wet-stiffening at increased dielectric-barrier discharge treatment levels are consistent with a covalent cross-linking mechanism. Increases in wet-stiffening do not appear at low treatment intensities. This is likely related to oxidation effects and surface cleaning to remove contaminants and extractives, which agrees with past studies in which low-pressure plasmas were employed. In closing, it is interesting to note that the cold-plasma treatment of bleached kraft pulps is accompanied with only minor changes in surface chemistry and yet these changes provide substantial and beneficial changes in physical properties. Further investigations will undoubtedly build on these studies and provide new fiber modification technologies to enhance the physical properties of this key renewable resource.

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