Eucalyptus fiber modification using dielectric-barrier discharge

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ABSTRACT: This study involves an investigation of the impact of the various levels of atmospheric dielectric-barrier discharge (DBD) treatment on the surface of eucalyptus fibers at different levels of beating with the objective of enhancing paper strength properties. The DBD treatment led to significant improvements in wet-strength tensile properties, increasing them by 2%-112%, as a function of the dosage of atmospheric plasma applied. Also, using controlled dosages of the DBD treatment, dry-strength tensile could be improved, reaching a 58% increase. In addition, non-beaten samples showed greater increases in strength properties than the beaten samples. Moreover, the acid surface content was unaltered by the DBD treatment, perhaps due to over-oxidation and generation of low molecular weight species that are easily removed by washing with water. Furthermore, increases in wettability could be observed for specific DBD dosage of treatments. Atomic force microscopy images of the treated handsheets showed that DBD treatment results in surface smoothing of the fibers. In conclusion, DBD treatment was shown to be an effective approach for eucalyptus fiber modification, especially in terms of enhancement of wet-strength properties.

Application: The cold plasma treatment studied here may contribute to the understanding of eucalyptus fiber modification.

Advances in papermaking and the physical properties of bleached kraft eucalyptus fibers have been applied to the production of paper grades previously made only with bleached softwoods. Eucalyptus is becoming one of the most important fiber sources for papermaking worldwide. It is predicted that by 2015, market pulp production will reach 70 million metric tons, with about 35 million coming from hardwoods and 50% of this coming from eucalyptus [1]. Key papermaking properties include bulk, opacity, formation, softness, porosity, smoothness, absorbency, and dimensional stability [2]. In addition, the low production cost of eucalyptus pulp, mainly due to high forest productivity and pulping yields, supports these projected growth patterns.

Ongoing scientific and technical advances with eucalyptus fibers are directed at modifying fiber properties for specific paper properties. An important component in the development of new or improved lignocellulosic materials is the surface chemistry of the fiber [3]. A variety of methods have been developed for modifying the surface chemistry of cellulosic fibers. These include chemical treatments (oxidation applying hydrogen peroxide and ozone; enzymes), polymer adsorption (as xylan and carboximethylcellulose), ultrasound, and one of the most promising—use of an atmospheric cold plasma generated by dielectric-barrier discharge (DBD), especially in light of its versatility and potential practical application [4,5,6,7]. Plasma treatment has many advantages over conventional wet-chemical surface modification. It is a dry, environmentally-friendly surface modification, does not require energy-intensive drying processes, and little, if any, chemical waste or byproducts are formed [8].

Plasma is a state of ionized gas, consisting of excited atomic, ionic, molecular, and free-radical species. DBD is one of the most attractive practical means of generating cold plasma since it can be readily accomplished under atmospheric conditions, requiring little sample preparation, and it is an environmentally benign process [4,5]. DBD treatment is a process in which a voltage is applied across two electrodes, where at least one electrode is covered by an insulating material. Under atmospheric conditions, the applied voltage causes ionization of the air in the gap between the two electrodes, generating cold plasma. Reactive species are generated by electron collisions in the discharge initiating different reaction paths, leading to the production of reactive intermediates. These reactive intermediates provide a convenient resource for surface activation of polymeric materials, including cellulosics, resulting in surface oxidation, increased surface energy, and the generation of free radicals that can readily react with additives to generate new surface grafted material [4,9]. In this regard, plasma deposition can be used to create molecular monolayer coatings, which require very small amounts of raw materials. Typically, DBD plasma treatment is believed to oxidize only the surface of pulp fibers without altering bulk properties [10]. With a porous substrate such as uncoated paper, it has been shown that plasma treatment may also permeate to inner layers [11,12].

Improving the strength properties of paper products has been a long-term goal of pulp and paper research. It was demonstrated 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 wet strength properties for softwood based fibers [13,9]. In this regard, atmospheric DBD treatment provides a new method of enhancing the wet-strength tensile properties of kraft linerboard [14]. Studies have demonstrated that the wet strength of a fully bleached elemental chlorine free (ECF) kraft paper could be substantially increased, depending on the amount of power applied to a sheet, by approximately 70%-275% [13,3]. Furthermore, this treatment was shown to improve the wet stiffness of paper by approximately 138%-144%, as a function of the level of cold plasma treatment. These beneficial effects were not simply due to oxidative changes in surface fiber charge, but rather from fiber crosslinking [13]. Indeed, studies indicate that very low treatment intensities result in increased wettability due to surface oxidation, which leads to a small reduction in wet-tensile index. However, increased treatment intensity brings about diminished wettability due to covalent crosslinking, which leads to increases in wet-tensile index [15].

The ability to control fiber charge is known to be significant for controlling the properties of papermaking fibers. The specific bond strength between kraft pulp fibers can be enhanced by increasing the carboxylic acid content at the surface of papermaking fibers [16], while increased carboxylic acids throughout the fibers are known to contribute to fiber swelling [17]. Recent studies show that cold plasma can be used to initiate the *in situ* grafting of selected carboxylic acid additives onto fibers so as to increase fiber charge [18].

The use of plasma treatment enables studies of the influence of surface energy and its components on paper printability, since the treatment leads to minimal changes in the paper surface topography. Plasma activation increased the surface energy of the papers, and also the polarity of the paper surface due to the formation of oxygen containing polar molecular groups. Printing evaluation showed that plasma activation influenced both ink and water absorption properties, and led to faster ink-setting. Plasma activation, resulting in hydrophobic surface-sized paper, influenced the ink transfer, print gloss, and density by changing water absorption properties [19].

The purpose of this study is to gain a deeper understanding of the DBD effects on eucalyptus fibers, for use as a fiber modification technology to enhance papermaking strength properties of this valuable resource. The current study examines the impact of a DBD treatment on the surface of fibers at different levels of beating.

MATERIALS AND METHODS

Raw material

A commercial ECF fully bleached eucalyptus kraft pulp (1.72 kappa number, brightness of 90.3% ISO) with a 540 mL CFS, from Brazil, was employed in this study.

Pulp samples were beaten in a PFI mill at 1000, 2000, and 3000 revolutions according to TAPPI Standard Method T248 sp-08 "Laboratory beating of pulp (PFI mill method)." Freeness was measured after each refining level according to TAPPI Standard Method T227 om-04 "Freeness of pulp (Canadian standard method)." Handsheets (60 gm^{-2}) were formed from beaten and unbeaten samples according to TAPPI Standard Method T205 sp-06 "Forming handsheets for physical tests of pulp," and were conditioned for 24 h at 50% relative humidity (RH) and 25.0°C prior to DBD treatment.

DBD treatment

A Sherman Laboratory Treater Station was used for DBD treatment of the paper sheets at 0, 0.5, 1.0, 2.0, and 5.0 $kWm^{-2}min$. The treatment electrode was a ceramic coated aluminum electrode that applied a high voltage across a 1.5 mm gap containing the paper samples. The samples were mounted on an aluminum table, which acted as a ground electrode as it passed the sample under the treatment electrode at controlled velocity of 5 m/min. The 20 kHz GX-10 power generator was used to convert power to a high frequency alternating current by a HT3 high tension transformer for production of atmospheric plasma. The applied dose (D) was governed by the number of DBD treatments and was calculated by:

$$D = \frac{l * n}{w * v}$$

where l is the nominal DBD intensity (0.5-5.0 kW), n is the number of treatments (2-400), w is the electrode width (0.4974 m), and v is the moving table velocity (5 m min^{-1}). All treated handsheets were conditioned for 24 h at 50% RH and 25.0°C prior to physical testing.

Paper testing

Tear strength and burst resistance tests were performed according to TAPPI Standard Method T220 sp-06 "Physical testing of pulp handsheets." Both the dry and wet tensile strength index for samples of reference and treated cellulosic fibers were tested using a Model 1122 Instron tensile testing apparatus, according to TAPPI T220 sp-06 and T456 om-03 "Tensile breaking strength of water-saturated paper and paperboard (wet tensile strength)," respectively. In the wet tensile strength tests, the samples were soaked in deionized water for 2 s prior to analysis.

Polyelectrolyte titration

The polyelectrolyte titrations were performed using a MUTEK PCD-02 particle charge detector [20]. The pulp sample (0.50 g, o.d.) was diluted with 100 g of 0.001 N Poly-DAD-MAC and stirred with a magnetic stirrer for 2 h. During this time, the cationic polyelectrolyte completely neutralized the anionic charge in the pulp. The solids were removed on a #100 mesh nylon sieve, and the filtrate (10 mL) was pipetted into the cell of the MUTEK PCD-02 particle charge detector and titrated with 0.001 N PES-Na to the endpoint where the streaming potential reached 0 mV. The rate of titration was controlled at 0.1 mL/min. In addition, 10 mL of Poly-DADMAC solution was titrated with PES-Na to the neutral point to determine the blank value. The specific charge density of the sample was calculated by the following formula:

$$q = \frac{(V_p - V_b) * c * 1000}{w}$$

where q is specific charge density ($mmolkg^{-1}$); V_p is the volume of titrant used for pulp (mL); V_b is the volume of titrant used for blank (mL); c is the concentration of titrant ($molL^{-1}$); and w is the solid content of pulp (g).

Moisture absorption/retention

The moisture absorption/retention of the samples in deionized water was measured by means of the modified Tea Bag method [21]. A pulp sample (0.10 g) was added to a small bag made of Dexter nonwoven fabric (grade 7291), and then the bag was dipped into deionized water. After the indicated immersion time (2 h), the bags were removed from the solution, drained on a separate paper towel for 10 min, and weighed ($W_{immersion}$). Then, the teabags were placed in a centrifuge tube and spun for 10 min at ~780 RPM, after which the weight (W_{cent}) was recorded. Each bag was placed in a forced air oven (100°C-110°C) for 6-10 h, cooled in a desiccator, and quickly weighed (W_{dry}). For each set of samples analyzed, 3-6 blank teabags were run according to the same procedure, but without sample. For each of the blanks, averages for W_1, W_2, and W_3 were calculated:

$$W_1 = W_{empty} - W_{dry}$$
$$W_2 = W_{immersion} - W_{dry}$$
$$W_3 = W_{cent} - W_{dry}$$

Finally, the absorbent and retentive capacities of the sample were calculated by the following formulas:

$$\text{Absorbent Capacity} = \frac{W_{immersion} - W_{dry} - W_2}{W_{dry} - (W_{empty} - W_1)}$$

$$\text{Retentive Capacity} = \frac{W_{cent} - W_{dry} - W_3}{W_{dry} - (W_{empty} - W_1)}$$

AFM analysis

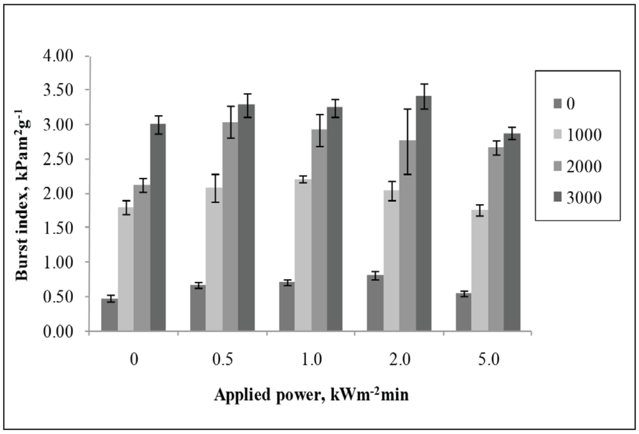
Atomic force microscope (AFM) analysis of paper test sheets was performed in air at room temperature in tapping mode over a 5 µm x 5 µm square using a 1-0 Ohm-cm phosphorus (n) doped Si tip, with a nominal frequency of 150 kHz and a nominal k value of 5 Nm^{-1}, on a Digital Instruments Nanoscope 3100 scanning probe microscope with a Nanoscope IIIa controller.

RESULTS AND DISCUSSION

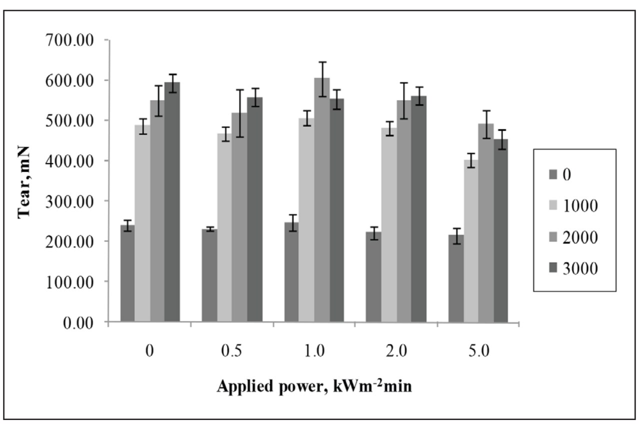
DBD treatment and physical properties

To evaluate the effects of DBD on the physicochemical properties of eucalyptus handsheets, a series of treatments were accomplished by varying the applied power from 0 to 5.0 $kWm^{-2}min$. Prior to DBD treatments, the pulps were subjected to different levels of beating—1000, 2000, and 3000—in an attempt to understand the impact of the DBD treatment on the fiber surfaces. Freeness values were 430, 320, and 240 mL CFS, respectively.

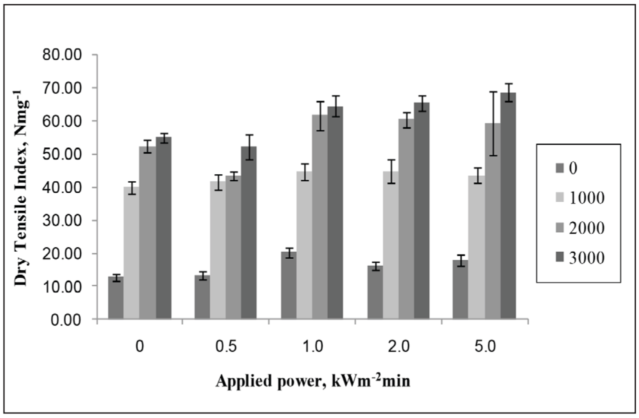
The results of treated and control handsheets, equilibrated at 50% RH and then analyzed for their tear, burst, and dry and wet tensile properties, are summarized in **Figs. 1-4**. Typically, the errors associated with these measurements of tear strength, burst resistance, and dry and wet tensile properties were ±4.65, ±2.10, ±6.51%, and ±4.17%, respectively. These results clearly demonstrate that DBD treatment can signifi-



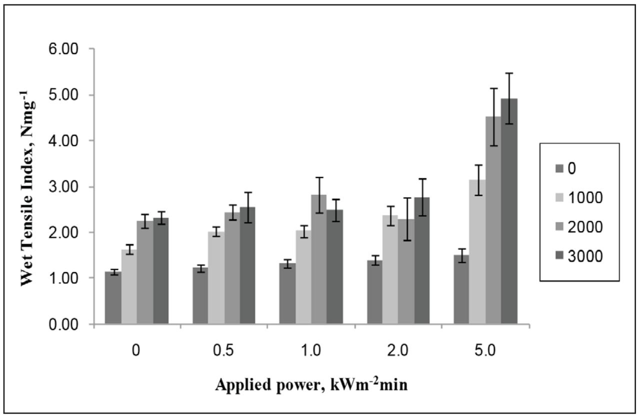
1. Burst index ($kPam^2g^{-1}$) for bleached eucalyptus kraft pulp fibers at various dielectric-barrier treatment dosages (0 to 5.0 $kWm^{-2}min$) and different beaten levels (0, 1000, 2000, and 3000 number of revolutions).



2. Tear (mN) for bleached eucalyptus kraft pulp fibers at various dielectric-barrier treatment dosages (0 to 5.0 $kWm^{-2}min$) and different beaten levels (0, 1000, 2000, and 3000 number of revolutions).



3. Dry tensile index (Nmg⁻¹) for bleached eucalyptus kraft pulp fibers at various dielectric-barrier treatment dosages (0 to 5.0 kWm⁻²min) and different beaten levels (0, 1000, 2000, and 3000 number of revolutions).

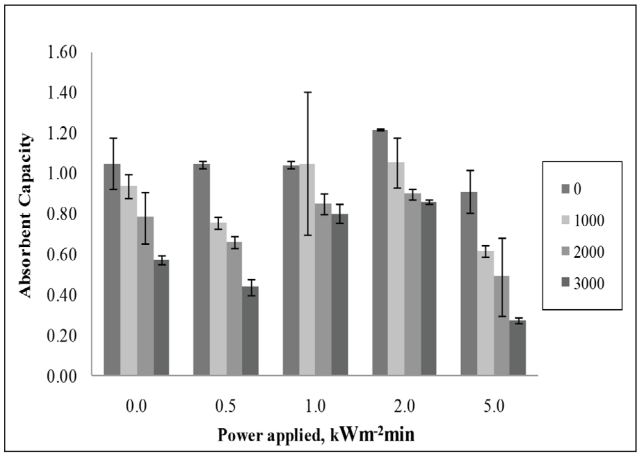


4. Wet tensile index (Nmg⁻¹) for bleached eucalyptus kraft pulp fibers at various dielectric-barrier treatment dosages (0 to 5.0 kWm⁻²min) and different beaten levels (0, 1000, 2000, and 3000 number of revolutions).

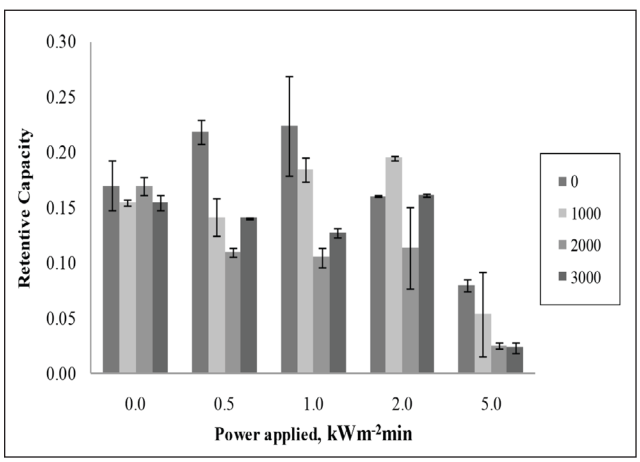
cantly improve wet tensile properties and that these benefits are proportional to the applied dosage of the DBD treatment. Enhancement by 2%-112% was observed for wet tensile, as a function of the dosage of atmospheric plasma applied. These data are in accord with previous studies from Johansson et al. [14], although it is significant to note that the prior studies were accomplished on a softwood kraft linerboard and this is the first example to demonstrate these benefits on short eucalyptus kraft bleached fibers. For dry tensile, the increase is lower, reaching a 58% increase for sample DBD treated at 5.0 kWm^{-2}min and beaten at 3000 revolutions. No significant differences were found for tear between the reference and treated handsheets (Fig. 2); however, the burst index showed an increase for some of the treated samples, especially those treated with DBD at 2.0 kWm^{-2}min (Fig. 1). As in accordance with Johansson et al. [14], for softwood kraft pulps changes in dry strength properties were much less than what were observed for the wet-tensile strength properties. Furthermore, it was found that all nonbeaten samples showed greater increases in strength properties than the beaten samples.

Polyelectrolyte titration and moisture absorption/retention

Polyelectrolyte titrations were performed for the determination of carboxylic acid content at the surface of eucalyptus pulp fibers over a wide range of DBD treatment power levels. For unbeaten and beaten at 3000 revolutions untreated samples, the fiber charges were 0.41 and 0.48 mmolkg^{-1}, while for samples DBD treated at 5.0 kWm^{-2}min, the values measured were 0.41 and 0.46 mmolkg^{-1}, respectively. Thus, our studies found no apparent alteration in carboxylic content with DBD treatment, perhaps due to over-oxidation and generation of low molecular weight species that are easily removed by washing with water, in accordance with Vander Wielen et al. [3]. Furthermore, improvements in strength properties can be supported by a cross-linking mechanism whereby the newly formed oxidized cellulose structures could contribute to fiber cross-linking via an acetal or ester linkage [9].



5. Absorbent capacity for bleached eucalyptus kraft pulp fibers at various dielectric-barrier treatment dosages (0 to 5.0 kWm⁻²min) and different beaten levels (0, 1000, 2000, and 3000 number of revolutions).

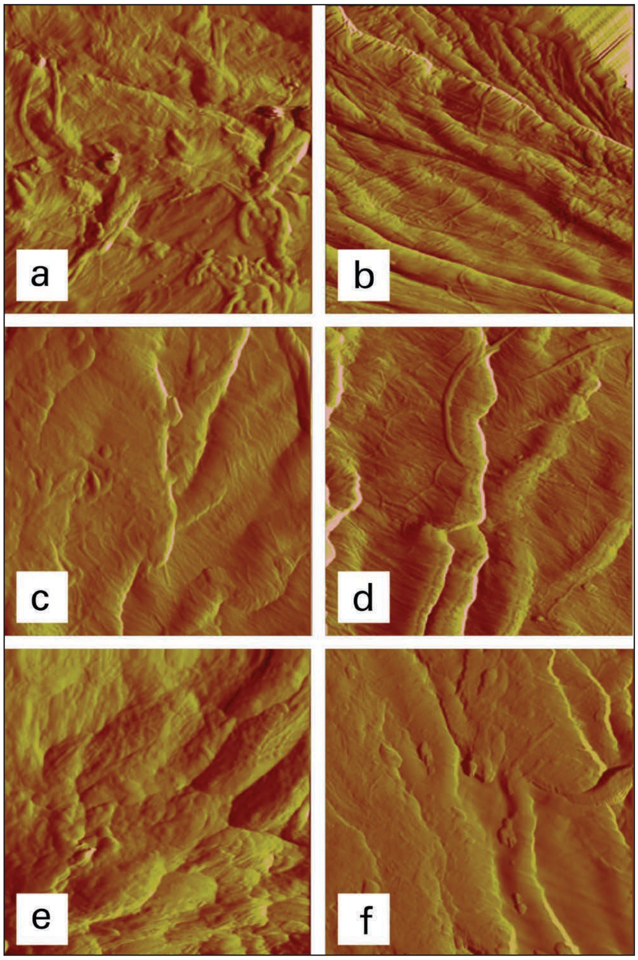


6. Retentive capacity for bleached eucalyptus kraft pulp fibers at various dielectric-barrier treatment dosages (0 to 5.0 kWm⁻²min) and different beaten levels (0, 1000, 2000, and 3000 number of revolutions).

Absorbent and retentive capacities (**Figs. 5** and **6**) were measured for DBD treated and control eucalyptus handsheets as a way to evaluate the ability of the fibers to absorb water. An increase in absorbent capacity can be seen in the intermediate levels of DBD treatment, whereas for the highest DBD level of treatment, the absorbent capacity decreases, followed by a dramatic decrease in retentive capacity. These data show the wettability increase found for intermediate levels of DBD treated samples, especially those treated with DBD at 1.0 $kWm^{-2}min$. Therefore, in papermaking, the DBD treatment under controlled dosage levels and, obviously, performing complementary investigation, could be used as an approach to help the grafting of specific additives, e.g., carboxylic acids, onto cellulosic fibers. In addition, improved water absorbency properties are especially important to avoid excessive use of superabsorbers [22].

AFM analysis

AFM was used as a tool to analyze differences in sample topography of the controlled and DBD treated fibers. AFM amplitude images of 5.0 µm x 5.0 µm scans are presented in **Fig. 7**, and they show the surface structure of eucalyptus fibers at various DBD treatment dosages and different beaten levels (0 and 3000 revolutions). As can be observed and as discussed in the following, the DBD treatment promotes changes in the surface morphology of the eucalyptus fibers. According to Mahlberg et al. [23], topographical changes in fibers by plasma activation are probably caused by different physical and chemical processes (e.g., etching, sublimation of new constituents that have been formed, and/or rearrangement of the chemically altered surface). The untreated fibers in Figs. 7a and 7b, both unbeaten and beaten at 3000 revolutions, show visible granular structures that have been attributed to amorphous material such as xylans, a major hemicellulose in eucalyptus pulp. Henriksson and Gatenholm [24] have proposed that absorbed xylan on chemithermomechanical (CTMP) pulp has a granular structure. Also, the granular layer is interpreted to originate from the middle lamella and the primary wall [25]. After the surface was treated with DBD, these granular structures are less apparent on the surface (Figs. 7c-7f). This surface "cleaning effect" by DBD treatment is in accord with previous observations from Vander Wielen et al. [3] and Johansson et al. [14]. Also, the DBD treatment seems to expose the S2 cell wall of nonbeaten eucalyptus fibers, as indicated by the presence of parallel fibrils (Figs. 7d and 7f). The same observation could not be noticed for beaten samples, possibly because of the fact that the beating process increases conformability of fibers by removal of the constraining primary layer of wood fiber, and fibrillates the fibers [26]. Indeed, for the highest power level of DBD, 5.0 $kWm^{-2}min$, the fibrils become indiscernible, appearing much more rounded and smooth.



7. Atomic force microscopy (AFM) amplitude images, 5.0 µm x 5.0 µm, of (a) bleached eucalyptus fibers treated at 0 $kWm^{-2}min$ and nonbeaten, (b) 0 $kWm^{-2}min$ and beaten at 3000 revolutions, (c) 1.0 $kWm^{-2}min$ and nonbeaten, (d) 1.0 $kWm^{-2}min$ and beaten at 3000 revolutions, (e) 5.0 $kWm^{-2}min$ and nonbeaten, and (f) 5.0 $kWm^{-2}min$ and beaten at 3000 revolutions.

CONCLUSIONS

Atmospheric dielectric-barrier discharge treatment proved to be very effective in regards to enhancing the wet-strength tensile properties of bleached eucalyptus kraft fibers. Moreover, under specific instrumentation conditions, dry strength could be improved. Otherwise, the acid surface content was unaltered by the DBD treatment, suggesting strength improvement due to fiber crosslinking. In addition, the wettability could be improved by controlling the DBD dosage level. Furthermore, results from AFM analysis demonstrated fiber surface modification by DBD, especially smoothing of the fibers. Conclusively, DBD treatment of eucalyptus fibers appears to be a valuable approach for papermaking fiber modification, mainly when wet-strength properties are required. **TJ**

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ABOUT THE AUTHORS

We chose this topic aiming to improve the knowledge of eucalyptus fiber modification, especially for paper production. In this context, cold plasma appeared as an interesting tool for improving strength properties, and no research on literature was found for eucalyptus.

This research complements previous studies developed by Ragauskas's group with regard to cold plasma treatment aimed at fiber modification. Previous studies did not evaluate hardwood, so with this study we complement previous ones by focusing on eucalyptus (hardwood) cold plasma treatment.

Once we were working with a short fiber (hardwood) some measurements were difficult, such as identifying wet strength, for example.

We found that modifying eucalyptus fibers with cold plasma treatment through dielectric-barrier discharge was possible; however, the results were not comparable to softwood.

By improving the fiber properties of paper, mills might see benefits in terms of machine runnability. The next step is to observe how application of cold plasma treatment to pulp instead of handsheets works. Thus, we may be able to evaluate the behavior of strength properties in the plasma treated pulps, in comparison to the treated handsheets.

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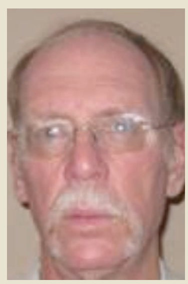

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