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Tailoring the Wet Strength of Linerboard Via Dielectric Barrier Discharge

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Abstract: Atmospheric dielectric-barrier discharge treatments were shown to be a facile and direct means of enhancing the wet-strength tensile properties of softwood kraft linerboard furnish. The improvements in wet-tensile strength were shown to vary between 10–190% depending on the charge of cold plasma applied. These benefits were accompanied with a minor increase in dry tensile strength and slight decrease dry tear strength and negligible changes in creep properties. AFM analysis of the treated sheets demonstrated that this treatment results in surface smoothing of the fibers.

Keywords: Linerboard softwood kraft pulp, dielectric barrier discharge, wet-strength, AFM

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INTRODUCTION

The need to modify fiber properties to yield specific paper properties has developed into a high priority research field, as well acknowledged at the recent 2001 Forest, Wood, and Paper Industry Technology Summit.^[1] In response to this industry need, a growing research effort has been directed toward influencing physical properties of paper via topochemical modifications. Early studies by Scallan and others demonstrated that fiber charge was a critical component in determining fiber swelling and an associated increase in paper strength.^[2,3] Ampulski pursued a similar line of investigation, examining the impact of the surface charge and bulk charge of CTMP fibers on tensile strength.^[4] These studies showed that tensile strength was increased proportional to fiber charge and suggested that surface charge provided a greater contribution to overall paper strength improvement. Engstrand et al. reported an increase in tensile strength, swelling, and sheet density^[5] by oxidizing spruce wood-meal and TMP with peroxide and oxygen. Studies by Barzyk et al. demonstrated that the placement of surface charge on a kraft fiber dramatically enhanced specific fiber-fiber bonding.^[6] Subsequently, studies by Laine et al. illustrated that the incorporation of CMC into kraft fibers led to substantial improvements of paper rupture properties, whereas elastic properties were less affected.^[7-9] In addition to these studies, several researchers have recently reported the use of specific oxidative treatments and grafting treatments that increase fiber charge and fiber-fiber bonding.^[10-12]

Along with these printing grade studies, research has been advancing new methods of modifying packaging grades of paper, including linerboard. Wong et al. have reported improvements in strength properties by pretreating fibers with cellulase.^[13,14] Studies by Chandra and Ragauskas demonstrated the ability to utilize laccase as a catalyst for surface grafting of high-kappa kraft pulps.^[15-17] This biografting treatment was shown to graft assorted charged and charge-neutral additives onto the lignin component of softwood kraft linerboard under ambient process conditions. Depending on the grafting agent employed, it was possible to increase the negative fiber charge by 50–100%, or alternatively, generate a fiber with a net positive charge. Physical testing of these biografted pulps demonstrated that these changes in fiber charge could yield distinct changes in physical strength properties including enhancements in burst, tensile, tear index, and most notably a 30–60% increase in wet-strength values.

In parallel to these biografting studies, work by Vander Wielen et al. has demonstrated that atmospheric plasma treatments provide a viable means of fiber modification and *in-vivo* fiber grafting.^[18,19] Although several studies have reported the application of corona and reduced pressure cold plasma to modify surface fiber properties, the use of a dielectric-barrier discharge generated atmospheric cold plasma for fiber modification is a relatively new field of study in pulp and paper.^[20-22] Interest in this technique has been

rapidly developing because of its ability to improve fiber properties and also because of its ease of practical application. Recent studies by Vander Wielen et al. have demonstrated that the wet-strength of a fully bleached ECF kraft and TMP paper could be increased by 60–150% depending on the amount of power applied to a sheet.^[18,19] Furthermore, this treatment was shown to improve the wet stiffness of paper as a function of the level of cold plasma treatment. Subsequent studies demonstrated that these beneficial effects were not simply due to oxidative changes in surface fiber charge, but rather come about from fiber cross-linking.^[23] These recent findings need to be further explored to evaluate their application to other grades of paper and to define the fundamental changes in fiber properties induced by dielectric barrier discharge (DBD). Along these lines, the need to enhance wet-strength and wet-stiffness of kraft linerboard is a well acknowledged field of study.^[24] This paper summarizes our efforts at utilizing dielectric barrier to enhance the wet-strength properties of virgin softwood kraft linerboard and determine the changes that occur to fibers upon exposure to atmospheric cold plasma.

EXPERIMENTAL

Chemicals and Materials

A commercial, southern U.S.A. pine, kraft linerboard pulp (103 kappa no.) with a 700 mL CSF was employed in this study. Prior to treatment, the kraft pulp was extensively washed until the wash water was pH neutral and colorless. All chemicals were commercially purchased and used as received.

Handsheets Formation and Dielectric-Barrier Discharge Treatment

Handsheets (121 and 212 g/m²) were formed using a standard British handsheet mold following TAPPI T205:2. The sheets were wet-pressed for 5 min and then restraint dried at 50% relative humidity. After drying, a Sherman Solid State Treater, a GX 10 Generator, and an HT3 High Tension Transformer (max output voltage 600 V R.S.M, operating frequency 20 kHz \pm 5%) were used in dielectric-barrier discharge treatment of the handsheets. The atmospheric cold plasma was generated in a 1.5 mm gap (air) between the dielectric barrier electrode and the aluminum table. The applied dose (D) was governed by the number of DBD treatments and was calculated by $D = I \cdot n / (w \cdot v)$, where I is the nominal dielectric barrier discharge intensity (0.1–1.0 kW), n the number of treatments (2–400), w the electrode width (0.4974 m), and v the moving table velocity (5 m/min). All treated handsheets were conditioned for 24 h at 50% RH and 25.0°C prior to physical testing.

Paper Testing

For the 121 g/m² handsheets, wet tensile testing was done after 5, 484, 719, 1022, 1523, and 4667 min of wetting. For the 212 g/m² handsheets wet tensile testing was done after 5, 193, and 378 min of wetting. Tensile strength tests were performed according to TAPPI T 456 om-03 and T 231 cm-96, with errors of $\pm 4\%$. Tear strength tests were performed according to TAPPI T 414 om-98. Zero span tests were performed according to TAPPI T 231 cm-96 and TAPPI T 273. Typically the errors associated with these measurements were $\pm 7\%$ and $\pm 4\%$, respectively. Creep studies were conducted using a tensile creep tester with an initial applied stress equivalent of 47% the tensile strength. Displacements were recorded using LVDT sensors with the output signals sent to a computer-based data system. A relative humidity of 50% was maintained for the first 18 h of creep testing and then increased to 70% for the remaining 12 h test period. Higher relative humidity values were examined after the initial 50% relative humidity creep tests did not indicate any difference between DBD treated and untreated handsheets.

AFM Analysis

AFM analysis of paper test sheets was performed at atmospheric pressure and room temperature in the tapping mode over a 5 micron by 5 micron square, with a silicon nitride tip, and resolution of 512 pixels by 512 pixels on a Digital Instruments 3100 Scanning Probe Microscope. Samples were held in place by double-sided tape. Test sheets were evaluated by imaging three positions on eight fibers for each treatment. Height, amplitude, and phase images were collected for each sample and the RMS roughness values for the height of each sample were determined.

RESULTS AND DISCUSSION

Physical Properties of Dielectric Barrier Discharge–Treated Linerboard

The results of treating 121 g/m² linerboard handsheets with varying doses of cold plasma, equilibrated at 50% relative humidity and then analyzed for their wet strength properties, are summarized in Figure 1. These results clearly demonstrate that treatment of linerboard handsheets with atmospheric cold plasma can significantly improve wet-strength properties and that these benefits are proportional to the applied dose of the dielectric-barrier treatment. The benefits of this treatment were shown to be sensitive to the time of wetting prior to wet strength measurements and the highest wet

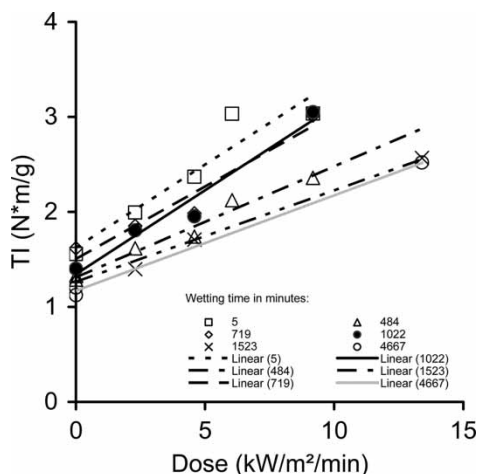


Figure 1. Changes in wet-tensile strength index (TI) for 121 g/m² handsheets of SW kraft linerboard before and after treatment with atmospheric dielectric-barrier discharge.

strength value was obtained for the shortest wetting time. Nonetheless, for the handsheets studied it is clear that the dielectric-barrier discharge treatment can enhance wet-strength values by 10–190%, dependent on the dose of cold plasma applied.

To determine if the dry-strength properties of the linerboard was changed due to the cold plasma treatment, the dry physical properties were also briefly examined, as summarized in Table 1.

These results suggest a slight increase in dry tensile strength at a low plasma treatment level and slight decrease in tear strength as the sheet is exposed to increasing amounts of cold plasma. These changes are, however, much less than what was observed for the wet-tensile strength properties. We briefly examined the effects of dielectric-barrier discharge on creep properties, and found that creep measurements for the 121 g/m² sheets

Table 1. Dry strength properties of linerboard sheets (121 g/m²) treated with dielectric barrier discharge

Dose (kW/m ² /min)	Tensile index (N*m/g ± 3%)	Tear index (mN*m ² /g ± 1%)	Zero span tensile index (N*m/g ± 2%)
0	49	14.0	103
4	53	13.8	111
8	48	13.3	103

showed no difference at 50% and 70% relative humidity for treated and untreated handsheets.

The results of wet-tensile testing for handsheets prepared at 212 g/m² are summarized in Figure 2. The overall trends remain the same as with the 121 g/m² handsheets. Improvements of >100% in wet-tensile index can be readily accomplished upon dielectric barrier discharge treatment.

AFM Analysis

Amplitude AFM analysis is a dynamic force microscopy mode where the cantilever-tip is excited at fixed frequency and the oscillation amplitude is used as a feedback parameter to image the sample topography. In phase imaging, the phase lag between the tip and the excitation signal is monitored and recorded while the feedback keeps the amplitude at a fixed value.^[25] The changes revealed by AFM phase and amplitude analysis for control and dielectric-barrier discharge treated fibers for the 212 g/m² sheets are summarized in Figure 3. The AFM phase and amplitude images on the surface of untreated kraft pulp fibers are in accord with previous observations.^[26–28] Although major breakdown of the cell wall is not indicated, the dielectric-barrier discharge-treated samples appear as if they may have undergone some surface cleaning. This is suggested by the fact that the small amount of granular type materials that appears on the reference sample is not observed among the dielectric-barrier discharge-treated sample.

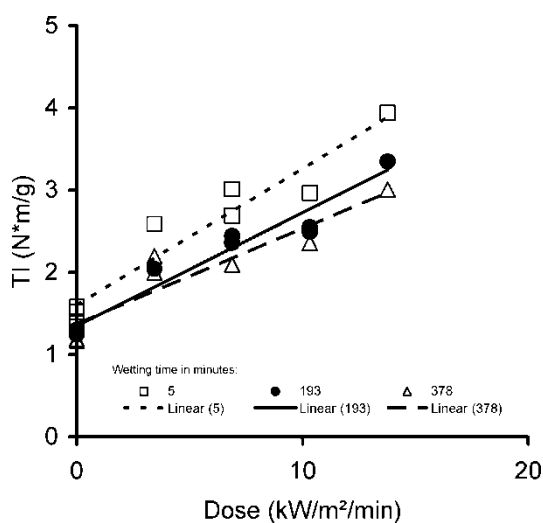


Figure 2. Changes in wet-strength strength index (TI) for 212 g/m² handsheets of SW kraft linerboard before and after treatment with atmospheric dielectric-barrier discharge.

Control

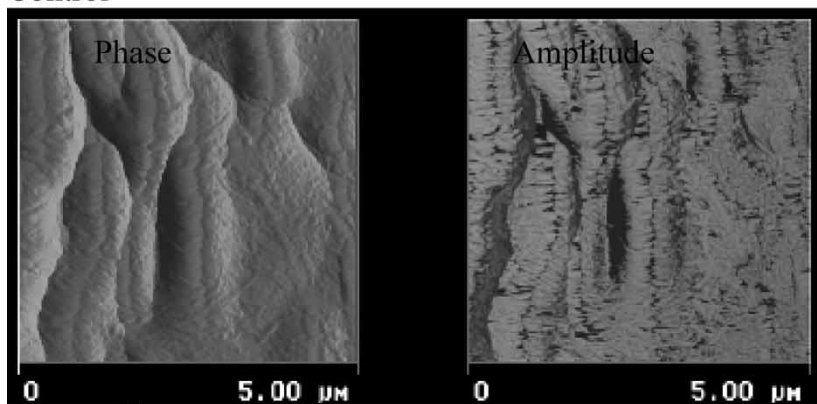
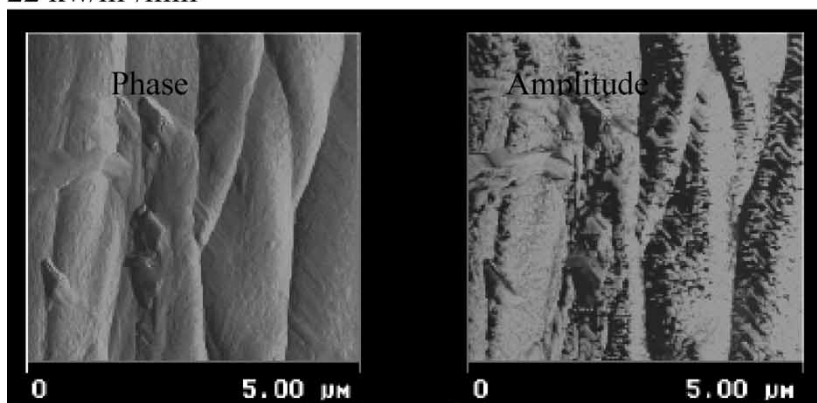
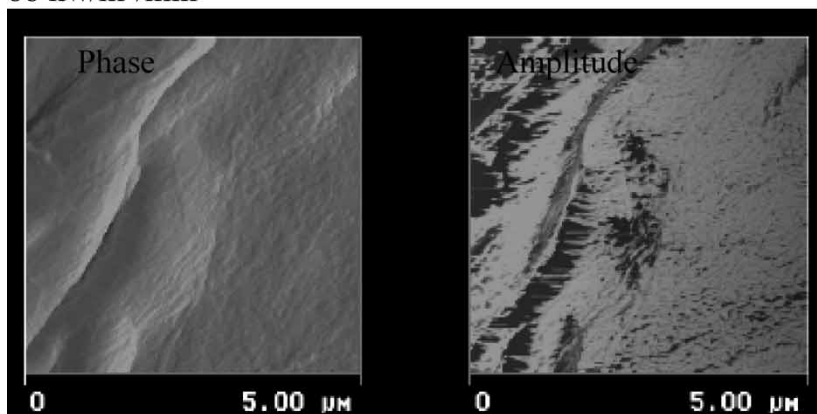
22 kw/m²/min88 kw/m²/min

Figure 3. AFM phase and amplitude images of control and dielectric-barrier discharge of 212 g/m² SW linerboard kraft sheets treated with 0, 22, and 88 kW/m²/min.

CONCLUSIONS

In summary, this study demonstrates that dielectric barrier discharge treatment provides a new method of enhancing the wet tensile strength properties of kraft linerboard. These treatments influence the fiber surface properties of kraft sheets and provide box manufacturers a new and promising technology. It is of significance to note that we have not yet determined an asymptotic limit to the benefits of atmospheric cold plasma treatment and wet tensile strength improvement. Recent advances in dielectric-barrier discharge theorem and equipment suggest that future improvements in this methodology will be quickly developed.

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