Mechanism of Dielectric-Barrier Discharge Initiated Wet-Strength Development

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ABSTRACT: The fundamental mechanism of wet-strength development for dielectric-barrier discharge treated thermomechanical pulp fibers was explored. Electron spectroscopy for chemical analysis (ESCA), vapor phase fluorine surface derivatization followed by ESCA, and dynamic contact angle analysis were performed to assess the surface chemistry in terms of both chemical functionality and wettability. Effects of the intensity of dielectric-barrier discharge treatment on the surface chemistry of lignocellulosic fibers and the corresponding impacts to fiber wet-tensile properties are described. This study indicates that 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. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2219–2225, 2005

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INTRODUCTION

Societal demand for products produced from sustainable resources via green chemistry continues to increase. This, in turn, drives industrial processes toward environmentally benign manufacturing technologies. The utilization of biomass feedstock, especially forest resources, has been recognized as a viable resource for innovative biomaterials.[1] The production of mechanical pulps is an example of an environmentally sustainable manufacturing process as it utilizes greater than the 90% of the wood biopolymers in an effluent-free process.[2] The resulting fibers consist mainly of cellulose, hemicellulose, and lignin biopolymers with small amounts of extractives and other materials. These fibers are employed in assorted products. Future applications of this bioresource are dependent upon developing innovative chemical modification processes that facilitate changes in the hydrophilicity, functionality, and distribution of chemical constituents on the surface of lignocellulosic fibers.[3–7]

The use of dielectric-barrier discharge as a surface treatment for synthetic and natural polymers has gained increasing interest due to its practical benefits and applicability.[8] The cold plasma generated from a dielectric-barrier discharge contains numerous highly reactive species including electrons,[8] hydroxyl radicals,[9] positive and negative oxidized ions,[10] reactive molecules[11] such as ozone,[8] and other excited species. Surface treatment with atmospheric plasma has long been associated with the increased surface energy and wettability of polymeric and lignocellulosic materials,[12–14] which has been attributed to the oxidative nature of the surface treatment.[15–18] However, recent studies indicate that treatment of lignocellulosic sheets at relatively high dielectric-barrier discharge treatment intensities results in smoothing of the fiber surface,[19] a decrease in water retention value,[20] and increases in wet-tensile index.[21] Typically, wet-strength is increased by covalent crosslinking or by protecting bonds in the sheet from the penetration of water.[22] However, the reported increases in wettability and surface oxidation associated with dielectric-barrier discharge treatment are not complementary to increases in wet-tensile. The purpose of this study was to investigate the changes in surface chemistry responsible for the development of wet-strength due to the dielectric-barrier discharge treatment of lignocellulosic fibers.

METHODS

Sample preparation

A commercially produced unbleached Norway spruce thermomechanical pulp was employed in this study. The pulp was fractionated, and the long fiber fractions (2.76 ± 0.049 mm) were isolated and formed into sample sheets without further refining, as previously described[18] to provide 60 gm^{-2} sheets with an average density of 0.220 g cm^{-3} ± 0.0041. The long fiber fractions were selected for surface analysis to avoid erroneously attributing experimental differences in the ratio of fines:long fibers[23-25] to experimental treatments.

Dielectric-barrier treatments

An atmospheric pressure, low-temperature plasma, known as a dielectric-barrier discharge, was applied to sample sheets containing 9.0% moisture, using a 15 kV GX-10 power generator attached to a Sherman Laboratory Treater with an HT-3 power transformer. The sheets were placed on the lower aluminum ground electrode. The plasma discharge was applied across an aluminum treatment electrode covered by a ceramic coating as the ground electrode carried the fiber web. By adjusting the ground electrode velocity and the watts applied across the treatment electrode, sheets were treated at 0, 0.10, 1.0, and 5.0 kW m^{-2}min. A portion of the plasma treated and reference sheets was extracted with acetone purchased from VWR in a Soxhlet apparatus for 24 h at approximately six cycles per hour prior to surface analysis.

Wet-strength analysis

The dry-tensile properties of samples cut to approximately 15.0 × 101.6 mm from reference dielectric-barrier discharge treated sheets were analyzed on an Instron Model 1122 instrument following Tappi Standard method T 494.[26] The wet-tensile properties of sheets formed from thermomechanical pulp fibers were also analyzed by Tappi Standard method T 494 after the strips were soaked in distilled water for 5.0 min and then immediately inserted into the clamps on the Instron apparatus.

Fluorination

A portion of the samples were fluorinated with trifluoroacetic anhydride (TFAA) purchased from Fluka to help to differentiate between hydroxyl and ether functionalities. The hydroxyl groups on the fibers were selectively labeled with TFAA vapor, at 35 °C for 45 min, using a method that has been previously described[27-29] and optimized[30] for use on lignocellulosic fibers. Samples were analyzed immediately following fluorination.

Surface characterization

ESCA studies were performed on reference and dielectric-barrier discharge treated samples that had and had not been Soxhlet extracted with acetone. In addition, samples of these sheets were fluorinated with TFAA and immediately analyzed by ESCA. All samples were degassed to 10^{-8} Pa and ESCA studies were performed on a Quantum 2000 instrument from Physical Electronics using a monochromatic Al Kα x-ray source (15 kV, 20.8 W, 100 μm beam size, 45° take-off angles, 500 μm analysis areas) and a neutralizer to avoid electrostatic charging.

Wettability studies

The wettability of acetone extracted reference and dielectric-barrier discharge treated TMP fibers was analyzed using the Wilhelmy plate technique on a Cahn DCA-332 dynamic contact angle analysis instrument, using distilled water and methylene iodide purchased from Sigma.[31] The advancing contact angles of distilled water and methylene iodide on the surface of 10 fibers at each condition were measured, averaged, and calculated by the harmonic mean method[32] to provide the polar and dispersive components of surface energy.

RESULTS AND DISCUSSION

Wet-strength analysis

To evaluate the effects of dielectric-barrier discharge on the physiochemical properties of TMP sheets, a series of treatments was accomplished by varying the applied power from 0 to 5.0 kW m^{-2} min. No statistically significant differences between the dry-tensile index of reference and treated sheets were observed. However, the wet-tensile index of dielectric-barrier discharge treated samples showed a small decrease at 0.10 kW m^{-2} min and then began to increase with increased dielectric-barrier discharge treatment (Fig. 1).

Surface chemical composition

Both reference and dielectric-barrier discharge treated TMP fibers were analyzed by ESCA. All spectra contained carbon and oxygen. In addition, several of the acetone extracted samples indicated traces of silicon, aluminum, or calcium at contents below 0.3%. The O/C ratios of the untreated samples, 0.60 and 0.58 for the extracted samples, are as expected, residing between the ratio of 0.49 expected for fibers with high
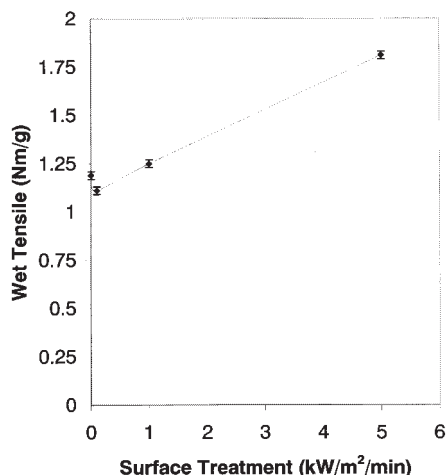
Figure 1 Wet-tensile index of reference and dielectric-barrier discharge treated sheets.

lignin contents[33,34] and 0.83 expected for cellulose.[27] Table I summarizes the chemical composition of various samples as analyzed by ESCA. The O/C ratio increased upon treatment in both unextracted and extracted samples. Extraction removes some oxidized species, which result in a lower O/C ratio overall for the surface treated samples.

Figure 2 shows high-resolution C1s spectra for each sample. The C1 peak in Figure 2(a–d) shows a marked decline with increased dielectric-barrier discharge treatment, compared to the deconvolution spectra for the acetone extracted samples shown in Figure 2–h. This is likely due to a reduction in the extractives present on the fiber surface with increased treatment. However, changes in extractives cannot account fully for the changes seen, as ESCA studies provide signs of surface oxidation among the acetone extracted fibers in the form of increased O/C ratios (Table I) and increases in oxidized functionalities; especially those arising from the C3 peak (carbon double-bonded, or

twice single-bonded to oxygen). Deconvolution of the C(1s) peak to study functional groups on the fiber surface can be elusive due to lack of resolution of the ESCA analysis, thus preventing further conclusions on the presence of oxidized species and their potential effect on wet strength improvement. Selective functionalization is an attractive means for gathering a greater understanding of the fiber surface chemistry.

Vapor phase fluorination with trifluoroacetic anhydride followed by ESCA was performed to quantify the amount of accessible hydroxyl groups at the surface of the plasma treated fibers. Table II shows the atomic composition for all the derivatized samples. Increases in the amount of incorporated fluorine were observed at low dielectric-barrier discharge treatment intensity levels and decreases in the amount of incorporated fluorine were observed at high levels. This indicates that the surface of the fibers contains more oxygen available as free hydroxyl groups at low dielectric-barrier discharge treatment and less oxygen available as free hydroxyl groups at high dielectric-barrier discharge treatment intensity. Figure 3 shows the correlation between wet tensile and hydroxyl groups available for fluorination.

High-resolution total carbon C(1s) peaks were collected and deconvoluted to provide class 1 (C1) carbons, which are carbons bonded only to carbons or hydrogen; class 2 (C2) carbons, which are carbons bonded only to a single oxygen; class 3 (C3) carbons, which are carbon double-bonded to one oxygen or carbon single-bonded to two oxygens; and class 4 (C4) carbons, which consist of a carbon single-bonded to one oxygen and double-bonded to another(Tables II and III).[36,37] In the case of the fluorinated samples, a class 5 (C5) carbon peak is also resolved (Table III). This peak represents the CF_3 peak, which arises due to the selectively fluorinated hydroxyl groups, and represents that portion of the C2 carbons that are found only as hydroxyl, but not as ether functionalities.[37–40]

TABLE I
ESCA Atomic Composition and the Functional Groups Present on the Surface of Dielectric-Barrier Discharge Treated Thermomechanical Pulp Fibers

Sample and treatment (kW m^{-2} min)	O/C ratio	C1 (C—C, C—H) (%)	C2 (C—O) (%)	C3 (O—C—O, C=O) (%)	C4 (O—C=O) (%)
Unbleached TMP fibers					
0	0.602	25.7	59.4	11.8	3.2
0.10	0.619	20.0	61.6	15.0	3.3
1.0	0.708	18.2	61.9	16.3	3.6
5.0	0.708	16.3	62.7	16.7	4.5
Acetone extracted unbleached TMP fibers					
0	0.578	21.9	62.0	11.7	4.5
0.10	0.649	19.0	58.4	18.8	3.8
1.0	0.649	21.8	59.0	16.5	2.8
5.0	0.672	20.1	60.7	15.6	3.7

a. Reference

b. 0.10 kWm⁻²min

c. 1.0 kWm⁻²min

d. 5.0 kWm⁻²min

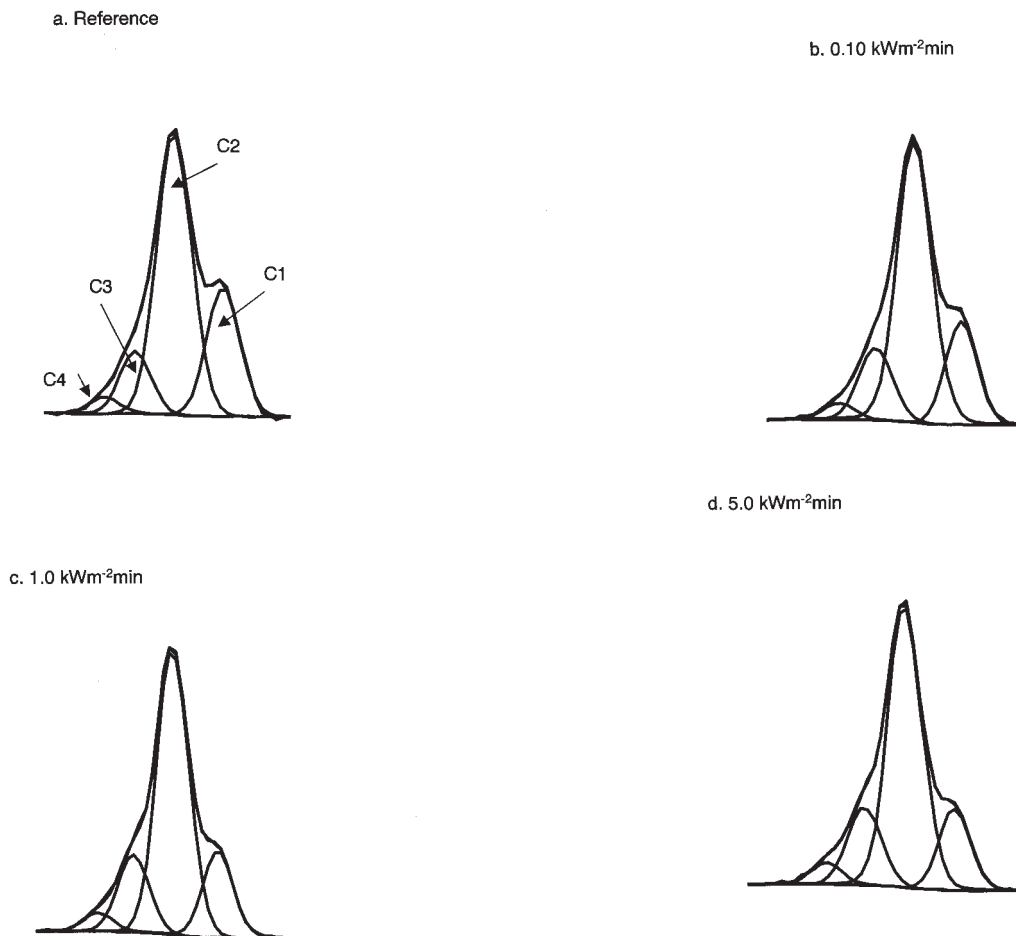**Figure 2**   ESCA C(1s) deconvolution spectra for TMP reference (a) and dielectric-barrier discharge treated (b) 0.10, (c) 1.0, and (d) 5.0 kW m^{-2} min samples and acetone extracted reference (e), dielectric-barrier discharge treated (f) 0.10, (g) 1.0, and (h) 5.0 kW m^{-2} min samples followed by acetone extraction.

It should also be noted that the C4 peak will contain data representing not only the C4 content of the fibers, but an additional C4 component; due to the reaction between the trifluoroacetic anhydride and the fiber, which inserts an ester functionality, as well as the CF$_3$ functionality upon reacting with the fiber surface (Table III).[30]

When examining the deconvolution spectra for samples upon which the hydroxyl groups were selectively fluorinated,[30] the peaks are much more easily resolved. When the integrations of these deconvolution spectra are compared, the C5 peak on the spectra for the fluorinated fibers that have not been extracted increases at low dielectric-barrier discharge treatment and decreases as treatment continues; indicating that the surface hydroxyl groups increase and then decrease. If the ratio of the C5 peak, which represents only surface hydroxyl groups, and the C2 peak, which represents hydroxyl and ether functionalities, is analyzed, this ratio increases with a low amount of surface treatment, but begins to diminish with increased treatment intensity (Table III). Hence, it is likely that

surface oxidation predominates at low treatment levels; while covalent crosslinking prevails at increased treatment intensities.

Wetting of dielectric-barrier discharge treated lignocellulosics

The wettability of single fibers randomly pulled by tweezers from the surface of reference and treated samples was studied using the Wilhelmy plate technique. Figure 4 shows tensiograms of untreated and dielectric barrier discharge treated TMP fibers that have been acetone extracted. The advancing and receding tracks of the tensiogram for all TMP fibers show a hysteresis, which is typical for wood pulp fibers and reflects their chemical and morphological heterogeneity.[38,39] In addition to hysteresis, the amplitude in force varies along the fiber length as a result of the topography and variation in the fiber diameter.[40] The fiber wettability was measured as the advancing contact angle of 10 single fibers per sample in distilled

e. Reference

f. 0.10 kWm^{-2}min

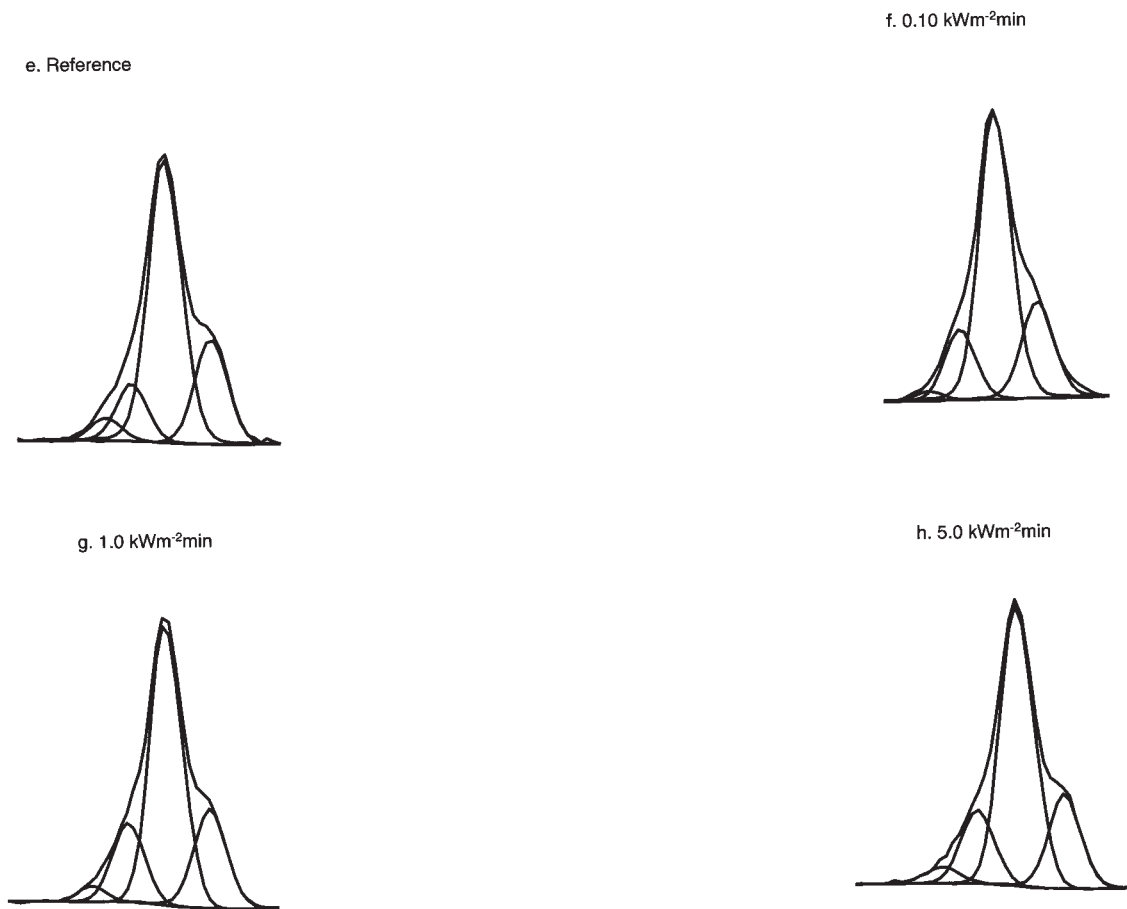g. 1.0 kWm^{-2}min

h. 5.0 kWm^{-2}min

Figure 2 (*Continued from the previous page*)

water and averaged (Table IV). The advancing contact angle indicated increased wetting with low dielectric-barrier discharge treatment, which began to diminish at higher treatment intensities. The polar and dispersive components of surface energy were calculated using the measured advancing contact angles of water and methylene iodide on single fibers via the harmonic mean method.[32] The polar component of surface energy appears to be the major contributor to the increased surface energy at low dielectric-barrier dis-

charge treatment levels, which correspond to increased surface oxidation (Table I), decreased wet-tensile strength (Fig. 1), and increased wettability (Table IV). This effect appears to diminish as the surface energy begins to decrease and the advancing contact angle begins to increase at increased dielectric-barrier discharge treatment intensity levels (Table IV). These results correspond with the decrease

TABLE II
TFAA Derivatization followed by ESCA

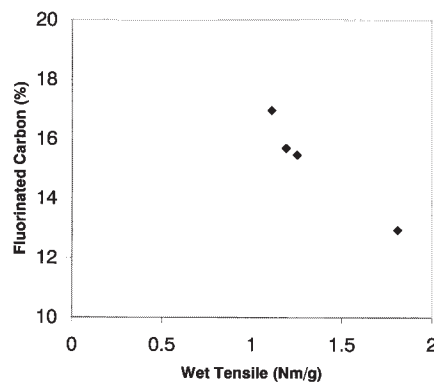| Sample and treatment (kW m^{-2} min)	C(1s) (%)	O(1s) (%)	F(1s) (%)
0	51.7	32.7	15.7
0.10	51.2	31.8	17.0
1.0	52.0	32.6	15.5
5.0	53.7	33.3	12.9
0	50.9	32.4	16.7
0.10	50.4	32.5	17.1
1.0	51.0	33.1	15.9
5.0	53.1	33.3	13.6

Figure 3 Surface hydroxyls available for fluorine derivatization versus wet-tensile.

TABLE III
TFAA Derivatization followed by ESCA to Study the Relationship between Wet-Tensile Strength and the Functional Groups Present on the Surface of Dielectric-Barrier Discharge Treated Thermomechanical Pulp Fibers

Sample and treatment (kW m^{-2} min)	C5/C2 ratio	C1 (C—C, C—H) (%)	C2 (C—O) (%)	C3 (O—C—O, C=O) (%)	C4 (O—C=O) (%)	C5 (C—F3) (%)
Fluorinated TMP fibers						
0	0.138	18.6	49.4	14.7	10.5	6.8
0.10	0.192	17.4	46.7	15.5	11.6	8.9
1.0	0.186	17.1	46.5	15.2	12.6	8.7
5.0	0.127	19.4	49.4	14.0	11.0	6.3
Acetone extracted, fluorinated TMP fibers						
0	0.166	14.6	51.1	13.4	12.4	8.5
0.10	0.200	14.0	47.2	17.2	12.2	9.5
1.0	0.169	14.5	48.0	17.1	12.3	8.1
5.0	0.140	19.0	47.3	15.9	11.2	6.6

in hydroxyl groups available for fluorination and increased wet-tensile index (Tables II and III). This offers additional support for covalent crosslinking at increased dielectric-barrier discharge treatment intensities.

CONCLUSIONS

The degree of modification at the surface of lignocellulosic fibers and changes to surface chemistry were shown to depend on dielectric-barrier dis-charge treatment intensity. At low treatment levels, surface oxidation occurred and the fibers became more wettable, which contributed to a small decrease in wet-tensile index. With increased dielectric-barrier discharge treatment, fewer surface hydroxyls were present at the fiber surface as determined by availability for fluorination, decreased wettability, and increased wet-tensile index despite the increased oxygen contents suggested by the ESCA studies on nonfluorinated samples. These observations indicate covalent crosslinking on the sur-
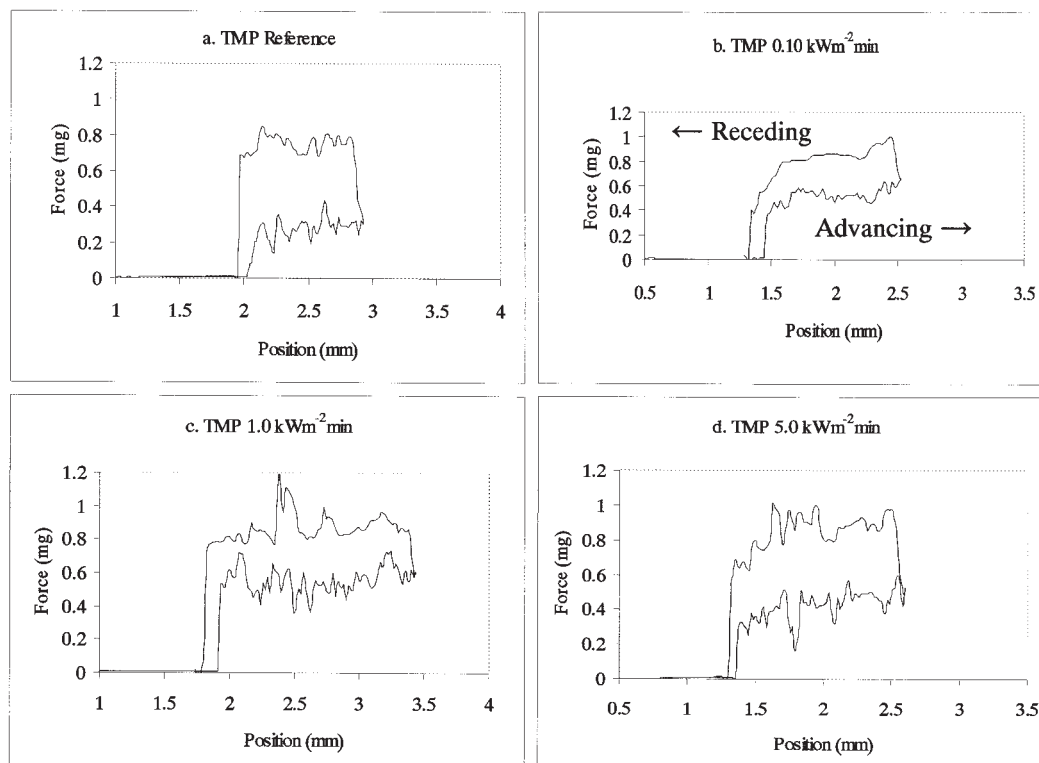

Figure 4 Typical tensiograms from dynamic contact angle analysis of TMP reference (a) and dielectric-barrier discharge treated (b) 0.10, (c) 1.0, and (d) 5.0 kW m^{-2} min fibers.

TABLE IV
Relationships between Wet-Tensile Strength and the Advancing Contact Angle in Water (θ_a) and the Polar (γ_p) and Dispersive (γ_d) Components of the Total Surface Energy (γ_{tot}) of Acetone Extracted Reference and Dielectric-Barrier Discharge Treated Thermomechanical Pulp Sheets

Sample treatment (kW m^{-2} min)	Wet-tensile (Nm/g)	θ_a (°)	γ_{tot}[a] (J m^{-2})	γ_p[a] (J m^{-2})	γ_d[a] (J m^{-2})
0	1.40	66.2	45.8	17.9	27.9
0.10	1.34	52.9	52.4	25.8	26.2
1.0	1.42	52.6	52.4	26.2	26.2
5.0	1.97	56.7	50.9	23.1	27.8

[a] Based an advancing contact angle measurements of single fibers with water and methylene iodine.

face of samples that were dielectric-barrier discharge treated at higher treatment intensities.

References

1. Singh, S. K.; Gross, R. A. In Biopolymers from Polysaccharides and Agroproteins; Gross, R. A., Scholz, C., Eds.; ACS Symposium Series 786: Washington, DC, 2001.
2. Johnston, P. A.; Stringer, R. L.; Santillo, D.; Stephenson, A. D.; Labounskaia, I. P.; McCartney, J. M. A. Towards Zero Effluent Pulp and Paper Production; Green Peace Technical Report 7/96: Exeter, UK, 1996.
3. Barzyk, D.; Page, D. H.; Ragauskas, A. J Pulp Paper Sci 1997, 23, J59.
4. Ström, G.; Carlsson, G. J Adhes Sci Technol 1992, 6, 745.
5. Batich, C. D. Appl Surf Sci 1988, 32, 57.
6. Felix, J. M.; Gatenholm, P. J Appl Polym Sci 1991, 42, 609.
7. Laine, J. T.; Lindstrom, T.; Nordmark, G.; Risinger, G. Nordic Pulp Paper Res J 2002, 17, 57.
8. Kogelschatz, U. Plasma Chem Plasma Proc 2003, 23, 1.
9. Naidis, G. V. J Phys D Appl Phys 1997, 30, 1214.
10. Shahin, M. M. Appl Optics Suppl Electrophotogr 1969, 3, 106.
11. Denes, F.; Simionescu, C. I. Cellulose Chem Technol 1980, 14, 285.
12. Back, E. L.; Danielsson, S.; Nordic Pulp Paper Res J 1987, 53.
13. Brown, P. F.; Swanson, J. W. Tappi J 2012 1971, 54.
14. Bezigian, T. Tappi J 1992, 75, 139.
15. Belgacem, M. N.; Blayo, A.; Gandini, A. J Colloid Interface Sci 1996, 182, 431.
16. Gurnagul, N.; Ouchi, M. D.; Dunlop-Jones, N.; Sparkes, D. G.; Wearing, J T. J Appl Polym Sci 1992, 46, 805.
17. Nishiyama, S.; Funato, N.; Sawatari, A. Sen-I Gakkaishi 1993, 49, 73.
18. Vander Wielen, L. C.; Ragauskas, A. J. Eur Polym J 2004, 40, 477.
19. Vander Wielen, L. C.; Elder, T.; Ragauskas, A. J. Cellulose 2005, 12, 185.
20. Vander Wielen, L. C.; Ragauskas, A. J. Invited book chapter in ACS Symposium Series, Modified Fibers with Medical and Specialty Applications; Edwards, V., Goheen, S. C., Buschle-Diller, G., Eds.; Kluwer, to appear.
21. Vander Wielen, L. C.; Page, D. H.; Ragauskas, A. J. Holzforschung 2005, 59, 65.
22. Espy, H. H. Tappi J 1995, 74, 90.
23. Pere, J; Lappalainen, A.; Kilijonen, K.; Tenkanen, M.; Mustranta, A. Eleventh International Symposium on Wood and Pulping Chemistry: Nice, 2001; Vol. 1, p 259.
24. Kleen, M.; Räsänen, H.;; Ohra-aho, T.; Laine, C. Eleventh International Symposium on Wood and Pulping Chemistry: Nice, 2001; Vol. 1, p 255.
25. Luukko, K.; Laine, J.; Pere, J Appita J 1999, 52, 126.
26. TAPPI Test Methods; Tappi Press: Atlanta, 1996.
27. Chilkoti, A.; Castner, D. G.; Ratner, B. D.; Briggs, D. J. Vacuum Sci Technol A 1190, 8, 2274.
28. Chilkoti, A.; Ratner, B.D.; Briggs, D. Chem Mater 1991, 3, 51.
29. Chtourou, H.; Riedl, B.; Kokta, B. V. J Colloid Interface Sci 1993, 158, 96.
30. Östenson, M.; Järund, H.; Toriz, G.; Gatenholm, P. Cellulose.
31. Miller, B.; Penn, L. S.; Hedvat, S. Colloids Surf 1983, 6, 49.
32. Wu, S.; Polymer Interface and Adhesion; Dekker: New York, 1982.
33. Börås, L.; Gatenholm, P. Holzforschung 1999, 53, 188.
34. Koubaa, A.; Riedl, B.; Zoltan, K. J Appl Polym Sci 1996, 61, 545.
35. Henriksson, Å; Gatenholm, P. Holzforschung 2001, 55, 494.
36. Gray, D. G. Cellulose Chem Technol 1978, 12, 735.
37. Dorris, G. M.; Gray, D. G. Cellulose Chem Technol 1978, 12, 9.
38. Johnson, R. E.; Dettre, R. H. J Phys Chem 1964, 68, 1774.
39. Berg, J. C.; Nonwovens, An Advanced Tutorial; Tappi Press: Atlanta, 1989; p 219.
40. Johnson, R. E.; Dettre, R. H.; In Contact Angle, Wettability and Adhesion; Fowkes, F. M, Ed.; Adv Chem Ser 1964, 43, 112.