Chapter 14

FIBER MODIFICATION *VIA* DIELECTRIC-BARRIER DISCHARGE
Theory and practical applications to lignocellulosic fibers

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14.1 Introduction

Given global emphasis on environmental awareness, the demand for innovative technologies that apply green chemistries to renewable resources for the 21st century will continue to grow [1]. The application of cold plasmas to wood fibers offers means to alter the surface chemistry and physical properties of one of the world's most abundant renewables. Plasma, the fourth state of matter, can be generated by a variety of methods including high heat conditions, the application of electromagnetic waves at radio and microwave frequencies in a vacuum, or when electrons in an electric current gain energy in amounts sufficient to separate gaseous atoms and molecules causing ionization.

The invention of the dielectric-barrier discharge device, which applies an electric current for plasma formation, is attributed to Werner von Siemens, who introduced the concept of dielectric-barrier discharge treatment of air for ozone generation in 1857 [2]. Today, dielectric-barrier discharges continue to be used for ozone generation [3] but have found applications in pollution control [4], silent discharge CO_2 lasers and ultraviolet excimer lamps [5], plasma displays [6], and the surface treatment of polymers [7]. The purpose of this review is to provide an overview of current and relevant research into the potential application of dielectric-barrier discharge to the surface modification of lignocellulosic fibers. Impacts of treatment in terms of the surface chemistry, physical strength properties, and water affinity of lignocellulosic fibers are discussed.

14.2 Dielectric-barrier discharge treatment

Dielectric-barrier discharge treatment involves a metal high-voltage treatment electrode, a ground electrode, and an insulating material covering at least one electrode to allow for the formation of glow discharges at atmospheric pressure, as opposed to the formation of one or several localized streamers [8]. However, the dielectric-barrier discharge is not without streamers as it contains numerous micro-discharges that exist for nanoseconds [9]. These micro-discharges increase in number as treatment power or time is increased while the properties of individual micro-discharges remain constant [5]. Surface treatment occurs when 10–30 kV are applied across 1–3 mm gaps between treatment electrodes, ionizing the air in the gap that appears as a visible violet–blue corona [5, 10–14]. Figure 14.1 typifies the surface treater used in our research studies, which is representative of industrial dielectric-barrier discharge configurations designed for the surface treatment of moving webs.

Dielectric-barrier discharge treatment applies a low temperature plasma of approximately 27–35 °C [13, 14] to materials. In our laboratory, the application of dielectric-barrier discharge treatments to paper sheets formed from ligno-cellulosic fibers in a 1.5-mm treatment gap caused sheet temperatures to reach as much as 40 °C at high treatment levels when samples were passed repeatedly across treatment electrodes at 5 m/min as measured by Thermography [15]. A maximum temperature of 36–40 °C was confirmed using Cole Parmer temperature indicator strips [15]. Cold plasmas for surface treatment can also be generated using radio frequency waves and microwaves, which require vacuum conditions. In contrast, dielectric-barrier discharges can be performed at atmospheric conditions, making dielectric-barrier discharge technologies advantageous from a practical standpoint [16].
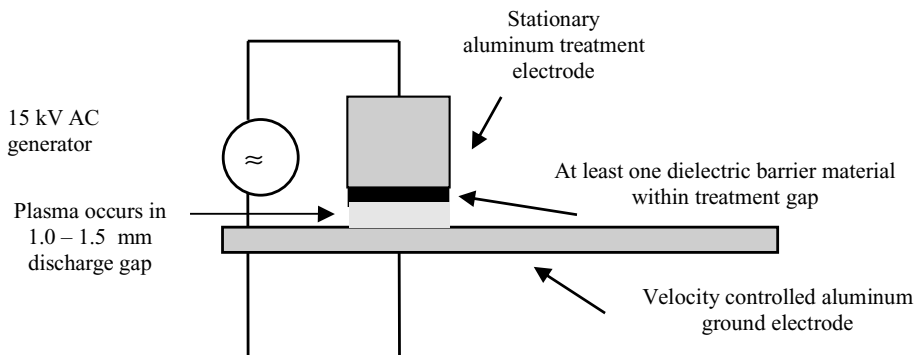

Figure 14.1. Schematic for a dielectric-barrier discharge treater

An atmospheric dielectric-barrier discharge plasma consists of photons [17], electrons [2, 5], free radicals [18], ions [2, 19], and excited molecules [20]. A major by-product of dielectric-barrier discharge is the production of ozone gas in the air [2]. When the high-energy electrons reach the surface of substrates, they have energies sufficient to break molecular bonds resulting in the creation of ions, free radicals, and other species on treated surfaces [10]. This leads to changes in surface energy, surface oxidation, cross-linking, broken bonds, disruption of surface layers, surface cleaning, and creation of free radicals on the surface of treated materials [10, 12, 21–23].

14.2.1 Physical and chemical modification of lignocellulosic fibers

Throughout the literature, dielectric-barrier discharge-initiated surface treatment is associated with increased surface energy and wettability as evidenced by the decreased contact angles of water on polymeric and lignocellulosic surfaces [23–26]. In our laboratory, the contact angle of nano-pure water on the surface of polyester film decreased from $65°$ to $30°$ with 0.056 kW/m²/min applied dielectric-barrier discharge treatment [15]. Decreased contact angles of water on the surface of cellophane with increased dielectric-barrier discharge treatment have been reported [25]. In our studies, the treatment of unbleached thermomechanical pulp fibers at low treatment dosages led to decreases in contact angle of approximately 12%; however, this effect diminished as treatment levels were increased (Table 14.1) [27].

Experimental difficulties measuring contact angles on rough, fibrous, and absorbent surfaces make inverse gas chromatography desirable for examining changes in the surface energy of lignocellulosic fibers [28–32]. Research studies reported that the dispersive surface energy of α-cellulose powder increased from 31.9 to 46.3 mJ/m² with corona discharge treatment [33]. However, the dispersive surface energies for dielectric-barrier discharge-treated bleached kraft and unbleached mechanical pulp fibers increase by 27.5% and 8.7%, respectively,

Table 14.1. Contact angles for dielectric-barrier discharge-treated fibers [27]

Treatment intensity (kW/m²/min)	Contact angle (°)
0.0	58.2
1.5	40.8
3.3	45.5
6.0	49.5
9.3	49.2

Table 14.2. Change in ratio of O/C detected *via* ESCA for dielectric-barrier discharge-treated fibers

Substrate	Percentage increase in O/C ratio due to surface treatment	Reference
Hardwood α-cellulose powder	10.1	[33]
Pine thermomechanical pulp	10.3	[15]
Spruce thermomechanical pulp (acetone extracted)	9.5	[27]
Bleached kraft pulp (acetone extracted)	2.8	[27]
Newsprint	20.5	[40]

with 0.12 kW/m^2/min applied dielectric-barrier discharge treatment [27]. As treatment intensity is further increased, the dispersive surface energies decrease until at or below those of untreated samples. This trend agrees with trends seen when the contact angle (Table 14.1) was investigated [27].

Electron spectroscopy for chemical analysis (ESCA) has been widely applied for examining the surface chemistry of lignocellulosic fibers [34–39]. The determination of surface O/C ratios *via* ESCA indicate that lignocellulosic materials are typically oxidized by dielectric-barrier discharge treatment (Table 14.2) [27, 33, 40].

ESCA studies regarding functional groups suggest that the measured surface carboxylic acid content of purified hardwood α-cellulose changes from 0% to 4.7% with dielectric-barrier discharge treatment while aldehyde groups increase from 12.4% to 19.9% [41]. Another study revealed increases in carboxylic acids of 0.04% in thermomechanical pulp sheets and 0.02% on Whatman filter paper, with respective increases of 0.58% and 0.98% among ethanol extracts that were attributed to an oxidative depolymerization and degradation process [21]. In our studies, an increase in surface carboxylic acids on bleached kraft fibers of approximately 45% occurred with 0.12 kW/m^2/min dielectric-barrier discharge treatment, with decreases of only 20% detected upon acetone extraction of treated samples due to the removal of degraded materials as detected *via* ESCA and surface titration methods (Table 14.2) [27, 42]. For dielectric-barrier discharge-treated unbleached thermomechanical pulp fibers, a 65% increase in carboxylic acid groups was measured before and a 23% net increase was measured after acetone extraction to remove degraded materials [42]. The spikes in surface acids at low treatment levels show a trend that is strikingly similar to the spike in dispersive surface energy seen at 0.12 kW/m^2/min [27]. In addition, the aldehyde content of thermomechanical pulp fibers was approximately doubled with dielectric-barrier discharge treatment [27, 42].
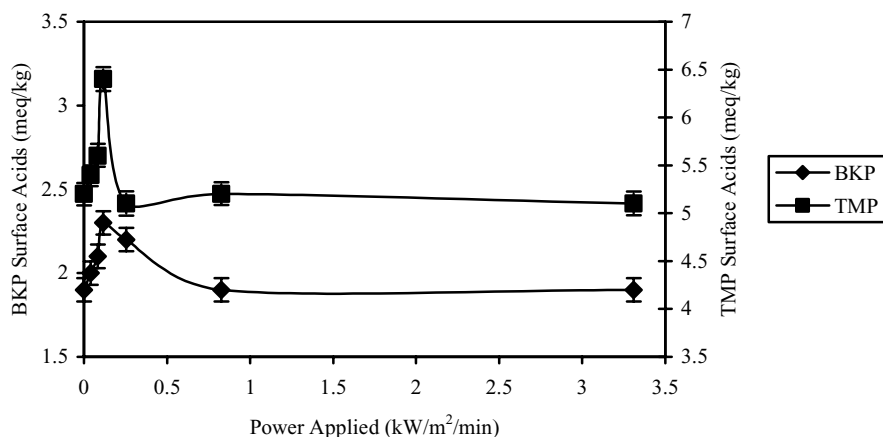
Figure 14.2. Impact of dielectric-barrier discharge treatment upon surface acid content
of fibers measured by polyelectrolye titration [27, 42]

Wet chemical methods using methylene blue dye, methylene violet dye, and Schiff's reagent followed by spectrophotometry, and the measurement of colorimetric nitrogen content were used to explore carboxyl and aldehyde groups. These methods indicated no increase carboxylic acid groups, and possibly a decrease, but did detect an increase in aldehydes [43]. The application of bulk conductometric titrations to fibers failed to detect changes in the carboxylic acid content of treated pulps [42]. The dye and conductometric titration methods measure the total acid groups, as opposed to surface acids. These methods are relatively insensitive to changes in the fiber surface acid groups since the large number of acid groups throughout the fiber may make it difficult to detect the impact of surface treatment. Nonetheless, detectable increases in surface acids were observed (Figure 14.2) when employing dielectric-barrier discharge treatment at low energy treatment dosages [27, 42].

Along with the surface chemistry effects of dielectric-barrier discharge on lignocellulosic fibers, several reports have documented changes to physical properties. The coefficient of friction of newsprint has been shown to increase with increased dielectric-barrier discharge treatment [40] while treated bleached kraft and unbleached thermomechanical pulps exhibited increases in the static coefficient of friction at low treatment levels, which reverse at high treatment levels (9.3 kW/m^2/min), as indicated in Table 14.3 [27]. Atomic force microscopy (AFM) images revealed a rough, fibrillar appearance at low dielectric-barrier discharge treatment, and a smoothing of the fiber surface at high dielectric-barrier discharge treatment, which was quantified using AFM to measure the root-mean-square (RMS) roughness [27]. The RMS roughness of bleached kraft and unbleached thermomechanical pulp fibers increased by

Table 14.3. Impact of dielectric-barrier discharge treatment on the static coefficient of friction (COF) and viscosity of lignocellulosic fibers [27]

Surface treatment (kW/m²/min)	COF for fully bleached kraft pulp	COF for unbleached thermomechanical pulp	Viscosity (cP) of bleached kraft
0.0	0.71	0.54	13.73
0.1	0.80	0.63	13.01
3.3	0.81	0.71	12.34
6.0	—	—	5.96
9.3	0.72	0.48	4.94

42% and 31%, respectively, at low treatment levels, then became smoother until roughness levels were similar to those of untreated samples as treatment intensity was increased [27]. Physical changes to cellulosic fibers were also reported in terms of pulp viscosity [27], which decreases as dielectric-barrier discharge treatment is increased (Table 14.3).

Damage to over-treated fibers, along with other property changes, can be seen when fibers are over-treated with dielectric-barrier discharge. Scanning electron microscopy (SEM) shows fibril damage and pin-holing at increased treatment levels [48]. In our laboratory, pin-holing of southern pine thermomechanical pulp sheets was seen at treatment levels at 0.13 $kW/m^2/min$ or greater [15], as illustrated by Figure 14.3. Recent studies report treatment of fibrous
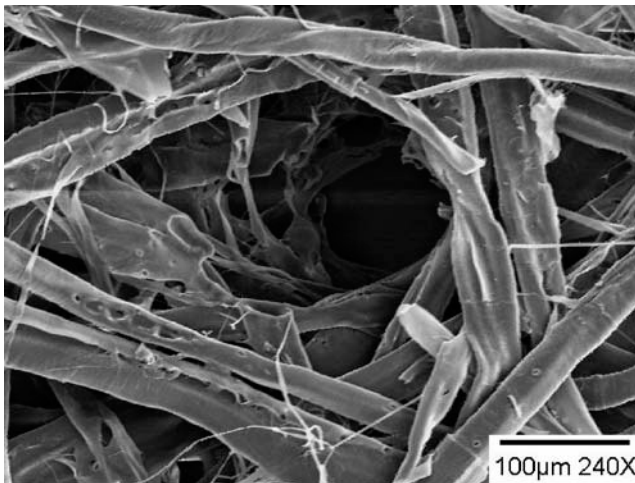

Figure 14.3. Pin-hole formed due to arcing in dielectric-barrier discharge system due to over-treatment of unbleached southern pine thermomechanical pulp fibers

Table 14.4. Change in brightness of dielectric-barrier discharge-treated fibers [15]

Surface treatment level, bleached kraft pulp (kW/m^2/min)	Brightness (%)	Surface treatment level, unbleached thermomechanical pulp (kW/m^2/min)	Brightness (%)
0.0	84.9	0	51.5
0.1	85.2	1.49	50.8
0.233	85.2	3.31	49.8
3.3	85.9	5.96	49.1
9.3	86.0	9.27	46.6

non-wovens involving the coverage of both electrodes by dielectric materials, rather than only one electrode, results in diminished pin-holing [44].

In addition, the brightness of bleached kraft fibers increases with dielectric-barrier discharge treatment while the brightness of unbleached thermomechanical pulp fibers decreases (Table 14.4) [15]. This is likely due to the surface cleaning of bleached kraft fibers [27] versus the oxidation of lignin on the surface of unbleached fibers to form chromophores [45].

14.2.2 Dielectric-barrier discharge induced grafting onto lignocellulosic fibers

An alternative application of dielectric-barrier discharge is to initiate grafting of materials onto lignocellulosics. Early studies into this avenue of research employed a two-step methodology [46]. In the first stage, a dielectric-barrier discharge was applied under reduced pressure (0.1mmHg) in the presence of nitrogen or air. The samples were subsequently immersed into an aqueous solution of ethyl acrylate. Untreated films showed no grafting, whereas treated films showed incorporation of up to 110% by weight at optimal conditions [46]. Dielectric-discharge treatment was also used to prime a fibrous cellulose sheet (Whatman filter paper) for grafting [47, 48]. After dielectric-barrier discharge treatment, styrene was grafted to the paper's surface in methanol. Optimal grafting occurred at a styrene concentration of 50%, with the bulk of grafting occurring in the first 30 s [48].

Our research group recently reported the dielectric-barrier discharge-initiated *in-situ* grafting of acryl amide [49] and maleic acid [50] onto lignocellulosic fibers. ToF-SIMS, SEM, elemental analysis, and titration methods showed that increased dielectric-barrier discharge treatment intensity results in increased grafting, that grafting occurs more abundantly on fully bleached kraft fibers than onto unbleached mechanical pulp fibers, and that grafting may be performed *in situ* rather than in a two-step process [49, 50]. When comparing
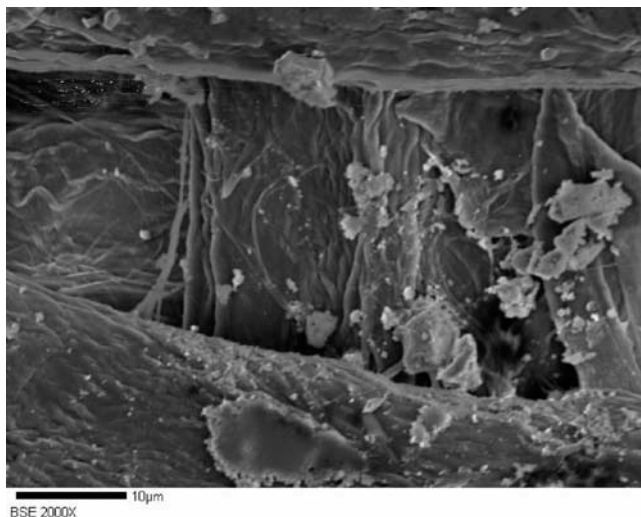
Figure 14.4. SEM micrograph of acryl amide grafted onto bleached kraft pulp fibers at 1.2 kW/m^2/min treatment taken at 2000$\times$

the *in-situ* and two-step grafting methods, the yield for the *in-situ* grafting is lower [46–50]; however, *in-situ* grafting can be performed quickly in a continuous web-fed process. Both methods result in grafting that appears to occur unevenly across the fiber surface [46–50]. The uneven grafting seen in our studies is described in Figure 14.4.

Given a high enough treatment dosage and sufficient monomer, the *in-situ* grafting process results in the formation of a composite material in which the grafted material coats the surface of the fibers [49] as described in Figure 14.5.

Two reaction mechanisms for dielectric-barrier discharge-initiated grafting onto cellulose in solution have been proposed [46, 48]. The "trapped radical" mechanism involves grafting to cellulose when monomers diffuse to react with trapped radicals within the fiber that become accessible in solution due to fiber swelling [46]. The other mechanism proposed is the formation of peroxides at the fiber surface, which would break down in solution when heat is applied, forming radicals in solution and on the fiber surface [48]. Bataille *et al.* [47] attributed the bimodal molecular weight distribution found when styrene was grafted onto cellulose film to a combination of both of these mechanisms. However, Sakata and Goring [46] found that when grafting ethyl acrylate to cellulose films, little to no homopolymer formed, and ferrous ion, which is known to catalyze the decomposition of peroxy species into radicals, actually inhibited grafting. For these reasons, they concluded that it was trapped radicals, rather than the formation of peroxides at the surface, which acted as grafting
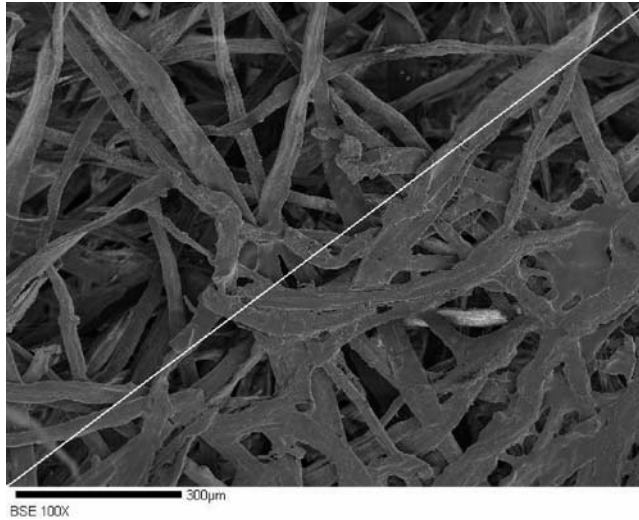
Figure 14.5. SEM micrograph of acryl amide grafted onto bleached kraft pulp fibers at 4.7 kW/m^2/min. Grafted (bottom right) versus unmodified fiber (upper left) are compared

initiators. In the case of *in-situ* grafting, the reactions are tentatively attributed to a free-radical mechanism [49].

14.2.3 Bonding of lignocellulosic fibers

The application of dielectric-barrier discharge to lignocellulosic materials for improved dry-strength performance was reported (1967) and patented (1969) by Goring [12, 51]. Pressing together layers of surface-treated cellulose acetate films or sheets formed from bleached hardwood and softwood kraft fibers increases the bond strength between laminates [11, 12, 43, 52]. The adhesion between treated laminates of wood, cellulose films, or paper with treated synthetic polymers can also be improved *via* dielectric-barrier discharge [11, 53]. Chemical additives impact this process, as the benefits to adhesion between paper and polyethylene upon surface treatment are enhanced in the presence of starch [54] while calcium carbonate fillers reduce adhesion [55]. Dielectric-barrier discharge is also applied to improving the adhesion of glues [56], paints [24], and inks [57] to lignocellulosic fibers. For example, the adhesion of toner ink to paper [57] can be enhanced by dielectric discharge in a photocopy machine.

When bleached kraft or unbleached thermomechanical pulp fibers were dielectric-barrier discharge treated over a wide range of treatment intensities (0–9.3 kW/m^2/min) and subsequently formed into sheets, the only significant improvements to bonding detected were increases in the wet-tensile index.

Table 14.5. Change in the wet tensile of dielectric-barrier discharge-treated fibers [59, 61]

Surface treatment (kW/m^2/min)	Wet-tensile index-bleached kraft (Nm/g)	Wet-tensile index thermomechanical pulp (Nm/g)	Wet-tensile index thermomechanical pulp (kNm/g)
0	0.53	0.67	0.045
3.3	0.71	0.86	0.073
6.0	0.83	1.17	0.090
9.3	0.91	2.53	0.111

Sheets formed from surface-treated bleached kraft and unbleached thermomechanical pulp sheets showed wet-strength increases of 20% and 60%, respectively [58, 59]. The dry-strength properties such as tensile, tear, and z-direction tensile remained unchanged. When fibers were grafted with monomers, such as acryl amide and maleic acid, followed by formation into sheets, similar results were observed [50, 58].

It was reported that treated sheets formed from bleached kraft pulp fibers with and without added polyacrylamide showed increases in breaking length (dry-tensile strength) at treatment levels up to 3.2 kW/m^2/min, which diminished above this treatment level [60]. In our studies, the surface treatment of formed kraft and thermomechanical pulp sheets at treatment levels ranging up to 9.3 kW/m^2/min caused no statistically significant changes to dry-strength properties, including tensile, tear, and z-direction tensile [58, 59]. However, the wet-tensile index of bleached kraft and unbleached thermomechanical pulp sheets increased with increased dielectric-barrier discharge treatment (Table 14.5) whether or not polymers were added [58, 59]. Since the magnitude of increases seen without polymer were similar to those seen when polymer was added, the data reported in Table 14.5 reports only data acquired when testing fibrous sheets not containing polymer. Wet-stiffening of fibers is also seen with increased dielectric-barrier discharge treatment [61].

14.2.4 Water absorption of lignocellulosic fibers

The water affinity properties of lignocellulosics are also impacted by plasma treatment. Modification by means of carbon tetrafluoride plasmas [62], the plasma deposition of hexamethyldisiloxane [63], and the application of other water repellent additives provides hydrophobic fiber surfaces. The atmospheric dielectric-barrier discharge treatment of wood causes water uptake to increase while dielectric-barrier discharge treatments in methane and acetylene render the surface of wood more hydrophobic [64]. The volumetric swelling

Table 14.6. Impact of dielectric-barrier discharge on the water affinity properties of fibers [15, 27, 59]

Surface treatment level (kW/m^2/min)	TAPPI WRV at 900g	WRV at 225g	Percentage water uptake	Percentage change in linear dimensional stability	Vertical water wicking (cm/s^2)
Bleached kraft pulp					
0.0	0.93	2.93	0	0	0.66
0.1	0.97	3.04	11.50	−2.56	0.66
3.3	0.89	2.76	−2.59	17.59	0.69
9.3	0.84	2.66	−34.24	49.75	0.69
Unbleached thermomechanical pulp					
0.0	1.15	4.0	0	0	0.76
0.1	1.15	3.7	13.84	−16.67	0.92
3.3	1.14	3.4	−4.94	25.00	0.89
9.3	1.13	3.1	−57.77	82.30	0.85

of cellophane films increases by up to 80% with up to 5.0 min corona discharge treatment [25]. Both the water absorption of ply-bonded paper formed from corona-treated bleached kraft hand sheets and the moisture absorption of corona-treated bleached kraft pulp were lower than that of untreated reference samples [43].

Our studies indicated both hydrophilic and hydrophobic behaviors among dielectric-barrier discharge-treated lignocellulosic fibers depending upon treatment intensity (Table 14.6) [27, 59]. The water retention value (WRV), which is indicative of fiber swelling, was tested by both Tappi Useful Method 256 [65], which provides centrifugation at 900g, and an additional lower acceleration (225g) method [15]. The WRV tests, change in linear dimensional stability, and percent water uptake each indicated increases in the water affinity properties of bleached kraft pulp at low treatment levels, which diminished with increased treatment [27, 59]. However, water-wicking studies detected no statistically significant changes in the vertical wicking of bleached kraft fibers. The 225g WRV test, analysis of change in linear dimensional stability, change in percent water uptake, and wicking studies performed using thermomechanical pulp fibers also indicated an increase in water affinity properties at low dielectric-barrier discharge treatment levels, which decrease with increased surface treatment [27, 59]. The spikes in water affinity at low treatment levels show trends that are strikingly similar to spikes in surface acids, the dispersive surface energy, and surface roughness previously discussed. These properties also diminished with increased dielectric-barrier discharge treatment intensity.

14.3 Conclusion

Surface treatment *via* atmospheric dielectric-barrier discharge has shown great potential for modifying a series of chemical and physical properties of lignocellulosic materials. The observed wet-strength benefits realized when lignocellulosic fibers are dielectric-barrier discharge treated have obvious applications in the pulp and paper. In addition, the ability to graft acrylic derivatives onto fibers provides a tremendous opportunity for the generation of biocomposites. A notable feature of these treatments is they can be potentially performed in a continuous process without requiring vacuum conditions or special solvents. In addition, this process has been shown to tailor the surface topochemistry of lignocellulosic fibers by simply adjusting treatment dosages with and without chemical additives. Further research and development of dielectric-barrier discharge applications to lignocellulosic fibers will undoubtedly be developed, as it provides a green method for altering the surface chemistry of the world's most abundant renewable resource.

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