Dynamics of the wetting process on dielectric barrier discharge (DBD) treated wood surfaces

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Abstract

Protection and preservation of wood properties in exterior environments can only be ensured if the surface is coated with a paint or varnish. In our experiments a dielectric barrier discharge (DBD) was used as a wood surface pretreatment for improvement of the subsequent deposition of thin paint layers from solutions onto these surfaces. As the adsorption, interfacial interactions and adhesion of paints are strongly dependent on surface wettability, the dynamics of the wetting process was analyzed. The results show that the water contact angle decreases after the DBD treatment, proving a more wettable surface. Additionally, the spreading of paint solution on the DBD treated surface is more isotropic, showing a lower tendency to elongate along the wood fiber orientation.

Keywords: wood surfaces; dielectric barrier discharge (DBD); spreading; wettability.
1. Introduction

Wood is a lignocellulosic natural polymer used in many applications, including as a building material and for furniture, interior paneling, fuel, musical instruments, etc. In chemical terms, the wood can be defined as a three-dimensional biopolymer composite, comprising an interconnected network of cellulose, hemicellulose and lignin with small amounts of extractives and inorganics. Because of the presence of abundant hydroxyl functional groups, wood has a very high affinity for water and polar organic liquids. As a consequence, wood is vulnerable to attack by biological agents (microorganisms, beetles and termites), mechanical stresses and also to environmental conditions (humidity, temperature, sunlight, volatile organic compounds, heat). These unavoidable conditions may induce the loss of its initial properties with aging time, leading eventually to the deterioration or even the total degradation of the wood.

Generally, preservation of wood properties, enhanced durability and corrosion protection can be ensured if the surface is subjected to heat treatments [1-3], laser irradiation [4] or chemical treatments [5-7]. Moreover, the wood mechanical, barrier, optical and esthetical properties can be improved if the surface is painted, varnished, glued, laminated, etc. For example, by covering the wood surface with layers polymerized by electron beam [8], UV irradiation [9] or plasmas [10-12], a good protection of wood bulk properties is ensured.

Because of its known effects such as cleaning, crosslinking, activation and modification of surface chemistry, a plasma treatment is a convenient way to modify the surface wettability and therefore the coating adhesion, without altering the bulk properties of a polymeric material. Based on their effects in improving the adhesion characteristics of polymers, plasma treatments, including flames and corona discharges, are widely used in the printing and packaging industries, and similar effects are expected to be obtained on the surface of a natural polymer like the wood [1, 13-15].

Taking into account the above, we present here a surface treatment method for wood samples, based on a dielectric barrier discharge (DBD), working at atmospheric pressure in helium. The purpose of our treatment was to improve the wetting process and adhesion properties of wood for the subsequent deposition of thin
paint layers on these surfaces. We used samples of walnut and the wetting properties were tested after the DBD treatments by optical imaging and water contact angle measurements. The behavior of paint solution drop on walnut surfaces was analyzed in terms of wetted area and wetting uniformity.

2. Materials and Methods

2.1. DBD treatment

A dielectric barrier discharge (DBD) was used to improve the wettability of the wood surfaces. The experimental set-up consists of two electrodes (disc-to-plane geometry), with a glass plate (1mm thick) as dielectric barrier placed onto the ground electrode. The wood samples were fixed on the top of the glass plate and the inter-electrode gap was adjusted to 20 mm. A high voltage supply was used to deliver a voltage pulse with 9 kV peak-to-peak amplitude and 1.6 kHz frequency. The power dissipated in the discharge was 40 W and the typical voltage and current waveforms were recorded [16]. Treatments were performed in helium (spectral purity), at atmospheric pressure, introduced into the inter-electrode gap by a gas shower placed near the disc electrode, with a fixed flow rate (Q) of 150 mL/min. In all the experiments, treatment duration was 10 seconds.

In our experiments, samples of walnut (Juglans regia) were used, which were sectioned along the fiber direction and were free of defects. The selected type of wood belongs to hardwoods, which are characterized by their high strength and durability. The samples, size 5 cm × 5 cm and thickness 4 mm, were treated by DBD and stored at room temperature (25°C), in controlled humidity conditions (50% RH). The dynamics of the wetting process was studied within a maximum of a 30 minutes after the treatment. Measurements included 5 samples and were repeated in different, randomly selected surface regions.
2.2. Wetting process analysis

The dynamics of the wetting process and the spreading of liquids (water and paint solution) before and after the DBD treatments were studied by contact angle measurements.

The contact angles were measured before and after the treatments, at room temperature (25°C), using the sessile drop technique. For a convenient observation of the liquid drop and its time evolution, as well for the study of the wetting dynamics, an experimental arrangement similar to the imaging system proposed by Elliot and Ford [17] and Scheikl and Dunky [18] was used. A drop of liquid was deposited onto the wood sample using a Hamilton syringe and the three-dimensional images were recorded with three sets of microscopes and video cameras at various time intervals (Figure 1). The C1 and C2 cameras were arranged horizontally for measurements in the parallel and perpendicular directions with respect to the wood fiber orientation and the C3 camera was placed vertically. The images were analyzed using the ImageJ open-source software [19].

![Figure 1. Experimental arrangement for the wetting dynamics study: M - microscope, C1, C2, C3 - video cameras.](image)

The wetted area was fitted with an ellipse, centered on the (0,0) point of the Cartesian coordinate system:

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1$$  \hspace{1cm} (1)

where $a$ is the semi-major axis and $b$ is the semi-minor axis.
The spreading uniformity \( (U_{\text{spread}}) \) of the liquid was defined as the ratio between the semi-minor and semi-major axes of the ellipse:

\[
U_{\text{spread}} = \frac{b}{a}
\]  

An ideal spreading uniformity, corresponding to an isotropic spreading of a liquid onto a surface, is associated with the ratio 1, i.e. a circular liquid drop.

The contact angle measurements were made using 1 \( \mu \)L drops of distilled water and 10 \( \mu \)L drops of paint solution. The reported values were averaged for at least 10 measurements, with the measured values varying within \( \pm 2^\circ \).

We used a commercial paint for wood surfaces (EMALUX, produced by Kober, Neamt, Romania). The paint solution was prepared using a mixture of organic solvents (SOLVADIL D 509, produced by Vadova, Valcea, Romania) and the final concentration of the paint solution was 75 % v/v. A fresh solution was prepared before each experiment.

### 2.3. Experimental data analysis

When a liquid drop is placed on the wood surface, two simultaneous and competitive processes are expected to occur as a function of time: spreading onto the surface and penetration into the wood volume [20]. To describe these processes several theoretical models based on contact angle measurements have been proposed [21-23]. Thus, the decay process of the contact angle with time can be described using the so-called differential method, based on the following exponential equation:

\[
\theta = \theta_0 + A \exp(-Kt)
\]  

(3)

where \( t \) is the time, \( \theta_0 \) is the initial contact angle (at the moment \( t = 0 \)), \( A \) is a amplitude constant (corresponding to the difference between the initial and the saturation contact angle, for long times), and \( K \) is a decay constant, defining the rate of the process. All these constants depend on the wood characteristics.

In our study, we aimed to analyze the temporal evolution of the contact angle of water on wood surfaces.

We introduced the following equation to describe the time dependence of contact angle
\[ \frac{d\theta}{dt} = -(K_1 + K_2)(\theta - \theta_0) \]  \hfill (4)

with the solution as a sum of two exponential decay terms, associated with the two processes, i.e. the spreading and the penetration:

\[ \theta = \theta_0 + A_1 \exp(-K_1 t) + A_2 \exp(-K_2 t) \]  \hfill (5)

where \( \theta_0 \) is the asymptotic value of the contact angle at long times, \( A_1 \) and \( A_2 \) are the amplitudes, \( K_1 \) and \( K_2 \) the rates of spreading and penetration, respectively.

Taking into account the two processes involved in the wood wetting, spreading and penetration, the values of contact angles and their time evolutions were fitted with equation (5) (the continuous lines in Figure 2).

Figure 2. Time evolution of water contact angle onto walnut surfaces in perpendicular and parallel directions, with respect to fiber orientation (symbols – experimental data, continuous lines – fits with equation (5)). a: for untreated sample; b: for 10 s DBD treated sample.

3. Results and discussion

The DBD treatments of different surfaces may initiate different reactions between the free energetic species produced in the plasma bulk and the species present and/or created onto the surface [24, 25]. In these complicated reactions the photons from the plasma must also be considered. Moreover, after treatments some reactions may continue in atmospheric air and many other reactions are also possible. In light of the above, we expected to improve the wood surface wetting behavior by DBD treatments, as a basic condition...
for good adhesion between the wood substrate and an adhesive. Our results show that the time evolutions of spreading and penetration processes are different on the untreated and DBD treated surfaces (Figure 2). Thus, the absorption of water in the untreated surfaces takes place in about 2 minutes after drop deposition, whereas the water drops disappear in only 15-20 seconds on the treated samples and no contact angle can be measured. During wood wetting, two different processes can be separated: a very fast process corresponding to the spreading (characterized by $K_1$) during which the drop diameter increases rapidly, and a second one associated with the penetration ($K_2$), during which the drop keeps approximately the same diameter, but its volume decreases. This evolution is similar for all the analyzed samples, on both the untreated and treated surfaces. After the DBD treatments, the $K_1$ increases, probably due to a higher density of functionalized sites and a new surface texture (Table 1). A lower influence of the DBD treatment on the $K_2$ is expected since the treatments modify only on a few monolayers depth below the surface and the penetration process depends more on the structure in the depth of the wood fiber and its inhomogeneity. The small differences in $K_2$ values are within the limits of errors during the fitting procedure.

Table 1. $K_1$ and $K_2$ values (s$^{-1}$) calculated from the time evolution of the water contact angles (10 s DBD treatment) on walnut samples for parallel and perpendicular directions with respect to the wood fiber orientation (Figure 2).

<table>
<thead>
<tr>
<th>Direction</th>
<th>$K_1$</th>
<th>$K_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Untreated</td>
<td>Treated</td>
</tr>
<tr>
<td>parallel</td>
<td>0.314</td>
<td>1.292</td>
</tr>
<tr>
<td>perpendicular</td>
<td>0.153</td>
<td>2.124</td>
</tr>
</tbody>
</table>

As a direct application of our treatments we analyzed the time evolution of the paint solution drops on the walnut surface. The efficiency of DBD treatments was shown by the measurements of paint drop area and its time evolution (Figure 3). Paint drops spread more rapidly and covered higher areas on treated wood surfaces. The evolution of the paint drops versus time onto the surface permitted the evaluation of the uniformity of paint drop spreading ($U_{spread}$) based on the images recorded by the C3 camera (see Figure 1).
Thus, at the beginning, the paint drops are very close to a circular shape, having a $U_{\text{spread}}$ value close to 1. Because of the natural tendency to elongate along the fiber direction, a few seconds after deposition the drop shape becomes elliptical and the $U_{\text{spread}}$ decreases. This behavior is similar for both the untreated and treated surfaces, but the values of $U_{\text{spread}}$ are higher on the treated surfaces, suggesting a modification of the spreading process (Figure 4). This effect can be associated with surface functionalization induced by DBD, independent of the fiber orientation.

Figure 3. Time evolution of the paint solution drop area on the untreated and 10 s DBD treated walnut surfaces.

Figure 4. Time evolution of the paint solution drop spreading uniformity ($U_{\text{spread}}$) on the untreated and 10 s DBD treated walnut surfaces.
4. Conclusion

In our experiments, a DBD at atmospheric pressure in helium was used as a pre-treatment for the subsequent improvement of the deposition of paint layers on the wood surfaces. Samples of hardwood were used and the wetting process was investigated after the DBD treatments by measurements of contact angle, speed of spreading and its uniformity. The results show that the DBD can be very efficient in enhancing the wettability of the wood surfaces, without macroscopic modifications of wood surface aesthetics. The spreading speed and uniformity of spreading are also enhanced. An exponential equation for the contact angle variation as a function of time was introduced to estimate the dynamic of wetting. We found an increased spreading rate on DBD treated samples as a result of surface functionalization by the treatment. Therefore, the DBD treatment may be a very convenient technique in wood preparation for painting, bonding with adhesives and applying protective layers, etc. DBD exposure of 10 seconds is sufficient to modify the wood surface without altering its bulk properties. As the treatment is at atmospheric pressure it is possible to optimize the experimental arrangement for industrial use.
References