MODIFYING WOOD SURFACES WITH ATMOSPHERIC DIFFUSE COPLANAR SURFACE BARRIER DISCHARGE PLASMA

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Abstract. This study presents possibilities of influencing the surface properties of Sessile Oak (*Quercus petraea*), European Ash (*Fraxinus Excelsior*), Norway spruce (*Picea Abies*), and European Larch (*Larix decidua*) by a low-temperature atmospheric plasma treatment (diffuse coplanar surface barrier discharge [DCSBD]) in various conditions of the plasma treatment. Effect of mutual distance from the surface of the electrode to a plasma-treated wood surface (from 0-1.2 mm), effect of plasma treatment duration (3, 5, and 10 s) usable on industry lines as well as the effect of the atmosphere used during the plasma treatment (air, N_2, and CO_2) were studied. Effects of plasma treatment on the wood surface were evaluated by measurement of water droplet contact angle, which expressed changes in the surface polarity. Mutual distance from the surface of the DCSBD planar electrode to the surface of a treated wood sample plays a crucial role in the final change of the surface polarity. If the mutual distance is set in the range from 0 to 0.4 mm, the hydrophilization effect is reflected on the surface of treated wood. Increased polarity can be expressed by measuring the contact angle of water droplets. In this case, this is reflected by lower values of contact angles than those of the reference plasma-untreated wood samples. Conversely, by setting mutual distance within a range of 0.5-1.2 mm, the hydrophobization effect was observed, as demonstrated by the increase in the contact angle values of plasma-treated wood samples compared with the reference sample, which in this case was wood hydrophobization. Hygrophobization of the wood surface was unlike many other published experiments and was achieved without the addition of other specialty chemicals only by setting the appropriate mutual distance. Conditions for possible industrial use of the plasma modification for all tested wood samples were found.

Keywords: DCSBD plasma, modification, surface polarity, contact angle, wetting, hydrophilization, hydrophobization.

INTRODUCTION

Exterior wood is vulnerable when exposed to the weather. Therefore, windows, facades, and outdoor wood furniture need to be protected with varnishes or other protective coatings with new layers painted on every few years. European legislation (European Parliament 2004) dictates the use of water-soluble coating materials. This situation is a serious challenge for the European industry of wood handling (processing). Our approach is the application of atmospheric plasma treatment on the wood surfaces to activate them prior to coating and thus provide better conditions for good adhesion between the wood surface and coating. Possibilities that can be offered by the diffuse coplanar surface barrier discharge (DCSBD) plasma technology in the wood coating process were studied. Parameters of the surface properties of wood modified in plasma discharge, such as change of surface free energy, contact

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angle, or wettability, were studied at different conditions of plasma treatment. Measurements of wettability and surface free energy were performed in standard laboratory conditions. Wettability was measured as the water droplet contact angle with surface energy evaluation (SEE) system.

In recent years, plasma technologies have been at the forefront in industrial application and in the field of research and development of new opportunities for protection of wood products. Application of DCSBD plasma on lignocellulosic materials still has not been well explored. However, it has great potential to become an efficient tool in modifying surfaces. Plasma is a universal and efficient technique that is being used to activate surfaces of various polymeric materials. By producing high-frequency electrical discharge, it generates an ionized gas that can change the surface properties of a material it is in contact with. Plasma is very effective in modifying surface properties of various materials, especially wetting and adhesion. The advantage of surface activation is the possibility of changing the wetting and adhesion of materials, thereby improving the resistance of wood (lignocellulosic materials) to degradation.

In laboratory scale, the impact of DCSBD plasma has already been tested on glass fibers (Kováčik et al 2006), textile materials (Ráheľ et al 2000, 2003; Šimor et al 2002, 2003b; Černák 2004), foils (Šimor et al 2003a), paper (Černák et al 2003; Tóth et al 2007), and wood fibers (Hnát 2005; Beňová 2007; Nováková 2007; Ondrášková et al 2008; Szalay 2009).

EXPERIMENTAL METHODS

Wood samples used in this study were sessile oak (*Quercus petraea*), European ash (*Fraxinus excelsior*), Norway spruce (*Picea abies*), and European larch (*Larix decidua*).

Preparation of Samples

Before the plasma treatment, samples were stored in an air-conditioned room (50 ± 1% RH, temperature 23 ± 2°C) for 24 h. Subsequently, samples were sanded with sandpaper (grit 150). For measurement of contact angle and surface free energy, 70- × 15- × 40-mm samples were used.

Conditions of Plasma Treatment

For observation of the plasma treatment effect, a DCSBD (Fig 1) system was used with an adjustable power output up to 420 W, a planar source of low-temperature plasma (Šimor et al 2002). The DCSBD electrodes, consisting of 15 pairs of silver strip electrodes embedded 0.5 mm below

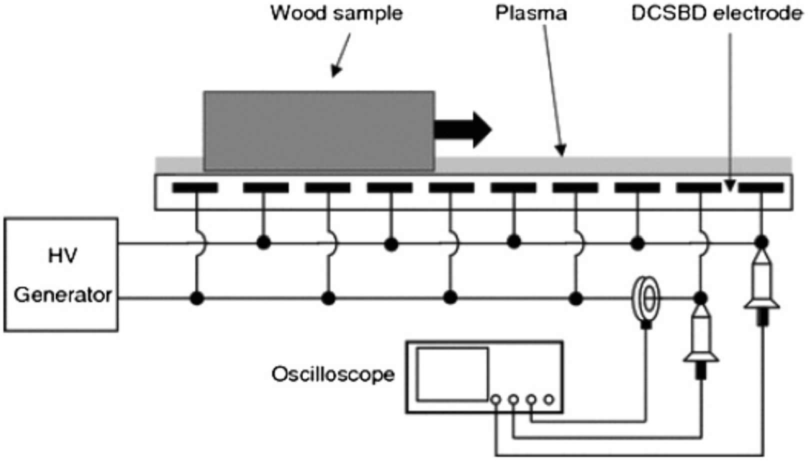

Figure 1. Diffuse coplanar surface barrier discharge (DCSBD) plasma experimental setup (Ondrášková et al 2008).

the surface of 96% Al_2O_3 ceramics, were energized by 14-kHz sinusoidal voltage supplied by an HV generator. The mutual distance of the 200-mm-long and 2-mm-wide silver strip electrodes was 1 mm.

Duration of the plasma treatment was set to 3, 5, and 10 s. Compressed air, N_2, and CO_2 were used as a working atmosphere. Effect of mutual distance from the sample surface to the DCSBD electrode surface (also called gap) was also investigated.

The mutual distance was adjusted by the stock of 0.13-mm-thick microscope coverslips from 0.13 up to 1.06 mm. Thickness of the individual plates was 0.13 mm.

Contact Angle

The SEE system was used to evaluate DCSBD plasma treatment for change of surface free energy. This system evaluates the surface free energy of the materials by measurement of the contact angle of liquids with different polarity. Changes of water droplet contact angle were monitored to express the impact of wood surface modification caused by plasma treatment from the specific distance from the surface of the electrode. This method optically reads the shape of the liquid droplet, which is applied on the surface of studied substances. Contact angle is defined as the angle that occurs between the planes of solid substance, tangent plane to the surface of the drop on solid interface with the surrounding atmosphere, and the droplet. The contact angle is function of the liquid's surface tension and the solid's surface energy. Various approaches have been developed to calculate the surface energy of solids from contact angle measurements (Chan 1994). The measurement of contact angles with different probe liquids is s common method to assess the hydrophilicity and wettability of a surface (Gindl et al 2001). In the present study, to assess the improvement in hydrophilicity and wettability of the wood surface, contact angle measurements were conducted with deionized water as the polar probe liquid. Contact angles of at least six drops were measured on each sample, and the resulting values in the figures and tables represent the average values of the contact angle in the graphs supplemented by the error bars.

RESULTS AND DISCUSSION

Figures 2-5 show dependences of the contact angle (θ,°) on the distance from the surface of

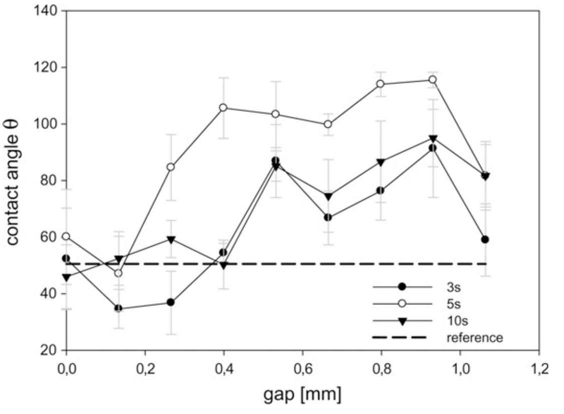

Figure 2. Effect of water drop contact angle changes on spruce wood treated in air atmosphere with diffuse coplanar surface barrier discharge plasma at various gaps (0-1.2 mm) and three different time regimes of plasma treatment (3, 5, and 10 s). Dotted line represents mean value of reference sample (plasma-untreated spruce wood).

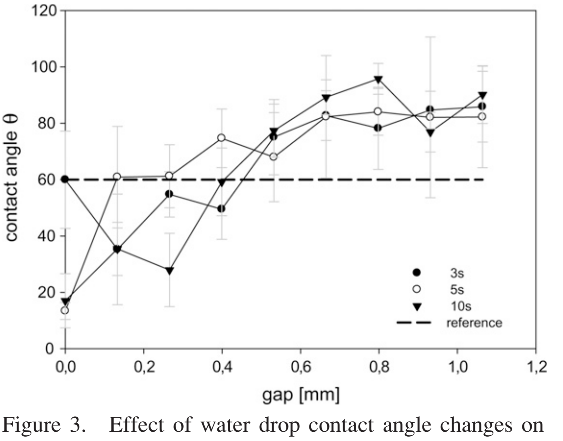

Figure 3. Effect of water drop contact angle changes on oak wood treated in air atmosphere with diffuse coplanar surface barrier discharge plasma at various gaps (0-1.2 mm) and three different time regimes of plasma treatment (3, 5, and 10 s). Dashed line represents mean value of reference sample (plasma-untreated oak wood).

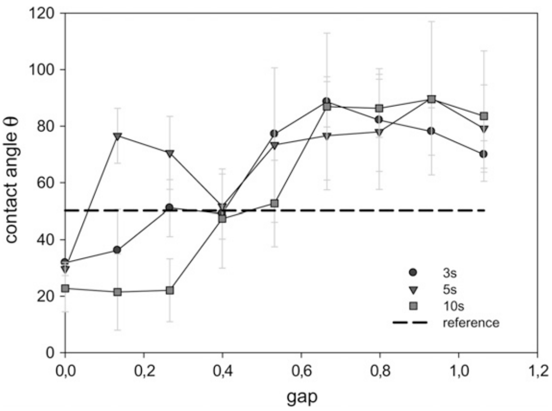

Figure 4. Effect of water drop contact angle changes on ash wood treated in air atmosphere with diffuse coplanar surface barrier discharge plasma at various gaps (0-1.2 mm) and three different time regimes of plasma treatment (3, 5, and 10 s). Dotted line represents mean value of reference sample (plasma-untreated ash wood).

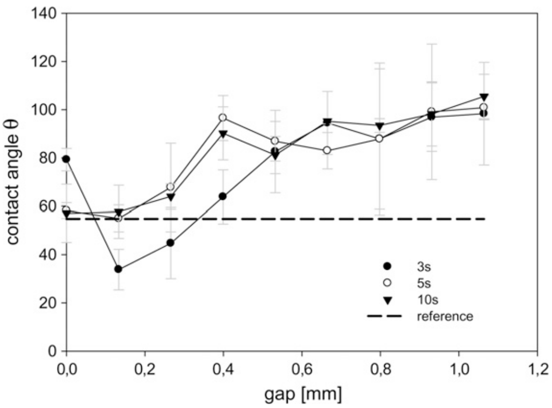

Figure 5. Effect of water drop contact angle changes on larch wood treated in air atmosphere with diffuse coplanar surface barrier discharge plasma at various gaps (0-1.2 mm) and three different time regimes of plasma treatment (3, 5, and 10 s). Dotted line represents mean value of reference sample (plasma-untreated larch wood).

the wood to the surface of the plasma electrode (gap, mm) during the 3-, 5-, and 10-s plasma treatment with the DSCBD in the air atmosphere for spruce (Fig 2), oak (Fig 3), ash (Fig 4), and larch (Fig 5) woods. At all time points of the plasma treatment, up to a distance of approximately 0.4 mm, the contact angle decreased compared with reference plasma-untreated spruce wood surface. The contact angle of water droplets on the reference spruce sample was 51.4°. Decreasing contact angle means that the surface of the wood became more hydrophilic than the reference plasma-untreated sample. In practical terms, this means that plasma treatment at shorter distances caused better wetting of the spruce wood surface. At distances greater than 0.5 mm, increasing contact angle was observed at all tested treatment durations, up to 0.9 mm. The surface then became hydrophobic.

The thickness of the generated DCSBD plasma layer was about 0.35 mm (Kováčik et al 2006). Direct contact of the wood surface and plasma layer in air atmosphere causes generation of polar chemical groups on the wood surface. However, increasing distance from the electrode causes the opposite behavior, and the wood surface becomes hydrophobic without needing to apply any additional chemical to the reaction system.

Table 1 summarizes the results of the maximum hydrophilizing and hydrophobizing effects on all tested woods caused by DCSBD plasma in air, CO_2, and N_2 atmospheres treated 5 s. Hydrophilizing and hydrophobizing effects were compared with reference plasma-untreated samples. As can be seen by changing the atmosphere, maximum hydrophobizing and hydrophilizing effects reached the various distances in all woods. Generally, at distances shorter than 0.5 mm, a hydrophilizing effect occurred in all cases, whereas at distances greater than 0.5 mm, a hydrophobizing effect took place. These changes

Table 1. Summary values of the distance from the wood surface to the surface of the plasma electrode for maximum hydrophilizing and maximum hydrophobizing effect caused by modification with diffuse coplanar surface barrier discharge plasma.

	Distance for maximum hydrophilizing effect (mm)			
	Oak	Ash	Spruce	Larch
Air	0	0.27	0	0.13
CO_2	0.13	0.13	0.13	0.13
N_2	0.13	0.13	0.13	0.13
	Distance for maximum hydrophilizing effect (mm)			
	Oak	Ash	Spruce	Larch
Air	0.80	0.93	0.93	1.06
CO_2	0.93	0.93	1.06	0.80
N_2	1.06	1.06	0.67	0.80

in the patterns of the wood surface were caused by reactions during plasma treatment, reflected by changes in the surface wettability as a result of formation of various types of functional groups on the lignin, hydrocarbons, or extractives. At shorter distances, generation of new polar groups caused hydrophilization of plasma-treated wood surfaces. Belgacem et al (1995), Lecoq et al (2008), Avramidis et al (2009), and Busnel et al (2010) found that plasma treatment results in formation of various functional groups such as aldehydes–ketones and carboxylic groups by means of electron spectroscopy for chemical analysis on plasma-treated samples of cellulose, lignin, and wood. These results were also confirmed by Calvimontes et al (2011). X-ray photospin spectroscopy analysis confirmed that plasma caused reactions, resulting in the decomposition of the polymer chain, oxidative reactions, and formation of aldehydes and carboxylic acids.

CONCLUSIONS

This study explored possibilities of wood surface modifications (sessile oak, European ash, Norway spruce, common larch) by DCSBD plasma in various atmospheres such as air, N_2, and CO_2 with different industrially applicable durations of plasma treatment (3, 5, and 10 s) and at various distances of the wood surface from the surface of the plasma electrode during plasma treatment. The atmosphere used for changing surface wettability of the wood affected surface properties of treated wood after plasma treatment. Air was the best industrially applicable atmosphere because it provides similar results to both other tested atmospheres but is considerably less expensive. Effect of the distance was essential for changing polarity of the surface. Generally, at distances less than 0.5 mm, a hydrophilizing effect occurred in all cases, whereas at distances greater than 0.5 mm, a hydrophobizing effect took place.

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