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IMPROVEMENT OF PLASMA TREATMENT EFFICIENCY OF WOOD AND COATING PROCESS BY SODIUM CHLORIDE AQUEOUS SOLUTIONS

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Abstract:
The results of this study showed that the appearance of discharge during treatment of wood with plasma highly depends on density distribution along the cross section of wood. By increasing the distance between the insulated high voltage electrode and substrate´s surface, the plasma streamers become more and more present in the regions of denser latewood, and at the some point these completely disappear. Modification of wood with differently concentrated NaCl aqueous solutions lead to an increased availability of ions, which improved the hydrophilic nature of wood surfaces and enhanced the effect of treatment of wood surface with plasma, making them even more susceptible to interact with water. However, the modification of wood with salt negatively affected on adhesion strength of applied commercial water-based coating. Further experimental work is planned to determine other dielectric properties of wood modified with NaCl, as well as detailed diagnostics of the discharges during plasma treatment.

Key words: *atmospheric plasma; wood; coatings; sodium chloride.*

INTRODUCTION

Wood coatings are used to protect the surface against photochemical deterioration and to maintain its desired appearance. But a proper preparation of the wood surface before the coating process is essential. For example, Suleman and Rashid (1999) reported that an improved protection of wood against deterioration can be improved by modification with various inorganic treatments prior to coatings applied. Another method for surface activation and enhanced wettability of lignocellulosic materials are electrical discharges (Chu *et al.* 2002; Žigon *et al.* 2018), and cold atmospheric plasma sources are the most useable due to their high productivity and low costs (Avramidis *et al.* 2010). The plasma treatment (PT) process causes physical-chemical transformations on the substrate’s surface, where enhanced interactions with applied liquids are the most beneficial (Král *et al.* 2015).

Dielectric Barrier Discharge (DBD) plasma is a special type of cold plasma, which can be used for treatment of wood surfaces (Žigon *et al.* 2018). Here, the substrate is placed in-between two high voltage electrodes, both connected to source of alternating current high voltage (AC-HV). A metal electrode is covered with a dielectric barrier preventing the formation of an arc discharge, excessive heat transfer, and thermal damage of the material (Kogelschatz 2003). The discharge is stable and more or less homogenous by smaller distances between the insulated electrode and substrates surface (i.e. gap distances) (Rehn and Viöl 2003). Space charges in the discharge gap generate many micro discharge channels (filaments or streamers), with typical diameters being 0.1 mm (Conrads and Schmidt 2000).

Beside the properties and conditions in plasma reactor, the appearance and other properties of the plasma discharge are highly dependent on the substrate’s inherent properties (De Cademartori *et al.* 2015), including its dielectric properties.

The knowledge and studies of the electrical and dielectric properties of wood are essential for its efficient use in many engineering applications (Şahin and Ay 2004, Şahin Kol 2009): the processes and the application of electrical energy for heating, drying, and gluing of wood, as well as for diagnostic purposes, e.g. measuring the moisture content and thickness of lumber, detecting defects, checking strength characteristics, estimating surface roughness by a nondestructive electrical measurement (Kabir *et al.* 1998; Skider *et al.* 2009; Zhou *et al.* 2013), and products like crossarms and poles for high voltage powerlines (Simpson and TenWolde 1999). Dielectric properties of a porous material like wood are affected by porosity, fiber direction, orientation of the electric field with respect to the structure, temperature, and air humidity (Norimoto 1976, Torgovnikov 1992, Duchow and Gerhardt 1996; Daian *et al.* 2005, Koubaa *et al.* 2008, Pentoś *et al.* 2017; Konopka *et al.* 2018). However, the main parameter influencing the conductivity of wood is the quantity of water in wood (Razafindratsima *et al.* 2017), which varies largely especially below the fiber saturation point (Simpson and TenWolde 1999, Romanov 2006, Otten *et al.* 2017).

When wood contains water-soluble salts or other electrolytic substances, its electrical conductivity substantially increases (Simpson and TenWolde 1999). Sodium chloride (NaCl) has been investigated as a protective agent against insecticidal and fungicidal effects. It was found that modification of wood by immersing it in a salt solution produces a surface protection. In the upper hygroscopic region, it also significantly influences the moisture content of wood, depending on the concentration and properties of impregnation solution (Hertel 1996; Lesar *et al.* 2009, Pařil and Dejmal 2014). Lesar and co-workers (2009) assumed that after modification of wood with NaCl, crystals are deposited in the cell walls and lumens, while the absorbed and free water in wood act as a solvent.

OBJECTIVE

In a previous study (Žigon *et al.* 2019), it was noticed that larger gap distances and unchanged energy supply resulted in visually more non-homogenous discharges and in streamers becoming more frequently present in the regions of latewood. Further increasing the gap distance reduced the number of streamers and the discharge volume, which eventually ceased completely.

The main objective of the present research was to evaluate the influence of the gap distance between the insulated HV electrode and the wood surface as well as the distribution of early and latewood on samples cross section on formation and intensity of the discharge. Presumably, the discharge appearance is greatly dependent on these factors.

As reported by Lima *et al.* (2017), an increase of NaCl concentration in aqueous solutions leads to a decrease of the pH and increased availability of ions H^+. This is most probably the reason that the dielectric constant of wood increases with the increase percentage on NaCl incorporated in its structure (Skider *et al.* 2009). Further, the equilibrium moisture content of wood increases with higher salt contents (Lesar *et al.* 2009), which is a major factor for the dielectric parameter of the material (Torgovnikov 1992). Therefore, this lead us to the second part of this study, which is presented in Figure 1. Firstly, spruce and beech wood were modified with application of differently concentrated aqueous solutions of NaCl to improve the appearance of the plasma discharge. The efficiency of such a process was evaluated via contact angles of water and of surface protective coating with modified and treated wood surfaces.

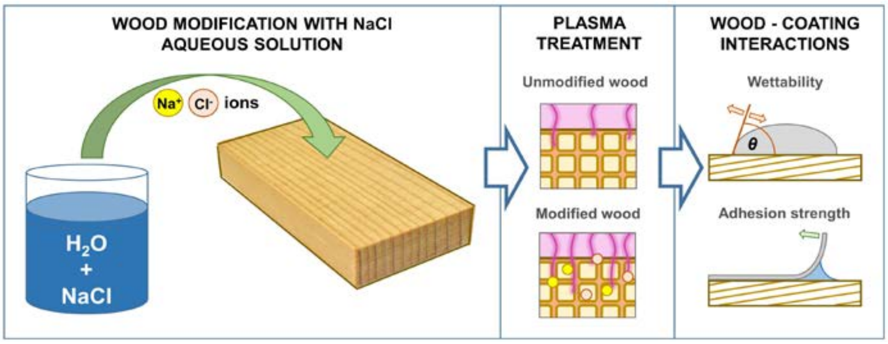

Fig. 1.
Schematic presentation of research objective.

MATERIALS AND METHODS

Samples of common beech (*Fagus sylvatica* L.) and Norway spruce (*Picea abies* (L.) Karst.) wood with dimensions of 60 × 30 × 15 were used in this study. All analyses in this study were performed on the samples surfaces with radial orientation of wood fibres. Samples were conditioned and stored at a temperature of 20°C and a relative humidity of 65%.

Solutions of NaCl (purity ≥ 99.5%, Honeywell, Charlotte, USA) in deionized water of five different concentrations (Table 1) were prepared and properly mixed until completely dilution of the solute. Wood samples were impregnated by dipping them in the solution for 3s.

The surface of each individual sample was treated using a Floating Electrode DBD plasma in air at atmospheric pressure (c.f. Žigon *et al.* 2019). The power supply delivered a peak voltage of 15kV at a frequency of 5kHz. The distance between the dielectrics was set to 5mm, the gap distance to 1 mm and the samples were fed at a moving rate of 3mm s^{-1}.

Table 1

Description of the NaCl aqueous solutions used in study

Designation	m NaCl [g]	m H_2O [g]	Mass fraction [%]	pH value
0	0	100	0.00	5.68
1.8	1.8	100	1.77	6.17
3.6	3.6	100	3.47	6.11
7.2	7.2	100	6.72	5.60
18	18	100	15.25	5.53
36	36	100	26.47	4.3

Study of discharge appearance

Discharge appearance, i.e. intensity of the discharge and distribution of plasma streamers, was observed with a Nikon D5600 (Nikon, Tokyo, Japan) photo camera (exposure time 1/20s, f5.6, ISO 5600). The intensity of light along the discharges were studied with function of grey scale with Fiji software (ImageJ 1.46d, Maryland, USA).

Water contact angle (WCA) measurements

WCAs of droplets of deionized water were measured using a Theta optical goniometer (Biolin Scientific Oy, Espoo, Finland). Water droplets with a volume of 5µL were applied on 6 different places of the radial surface on the each sample and the dynamic changes of their apparent CA were measured by Young-Laplace analysis using the software (OneAttension version 2.4 [r4931], Biolin Scientific), within 63s (1.9 images per second). Measurement started when the droplet was separated from the dispenser, which occurred approximately 2s after the first contact of the drop with the samples surface. In the case of PT samples, the measurements of CA were performed immediately after plasma treatment to avoid the effects of ageing.

Determination of colour changes

Colour of the samples' surfaces were measured using spectrophotometer X-Rite (USA) SP62 with the D65 type of light. Colour measurements were performed before and after modification with NaCl aqueous solutions, as well as after PT process performed, to monitor their colour changes after particular step of surface preparation. Total colour changes of samples surfaces (ΔE^*) after each step, in comparison to previous one, were calculated according to equation (1):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}\ , \qquad (1)$$

where: the parameters ΔL^*, Δa^* in Δb^* represent the changes between initial and end value of L^* (luminosity), a^* (red-green) and b^* (yellow-blue) coordinates in CIELAB colour space.

Formation and scanning electron microscope (SEM) analysis of the coating systems, adhesion strength measurements

Four types of larger specimens of beech wood species with dimensions of (300 × 75 × 3) mm^3 were prepared: Control, control-PT, NaCl impregnated, and NaCl impregnated-PT. On prepared samples, a 240µm thick film of water-based commercial coating (Belinka Interier, Belinka Belles, d.o.o., Ljubljana, Slovenia) was manually applied with a quadruple coating applicator.

The wood surface-coating interface was studied on the cross section of samples B-18 and B-36 with scanning electron microscope (SEM, FEI Quanta 250, FEI, Hillsboro, Oregon, USA). The micrographs were taken at 100 × and 500 × magnifications in a low vacuum (50Pa), at a voltage of 10.0kV, a spot size of 3.0, and a beam transition time of 45µs. Signals were detected and collected with Circular Backscatter Detector (CBS) or Large Field Detector (LFD), to get different information about the interfaces.

Adhesion of the coatings systems was evaluated by the pull-off tests of a coating films from the substrates 21 days after application, according to the standard EN ISO 4246 (2016). On the surface of each specimen in a series, 10 aluminium dollies with a diameter of 20mm were glued on the coated wood surface with a two-component epoxy resin. After 24h of curing, the perimeters of the glued dollies were carefully cleaned down to the substrate, to prevent propagation of failures out of the tested area. The adhesion strengths of cured films were measured by using the pull-off testing machine DeFelsko Positest adhesion tester (DeFelsko Corporation, Ogdensburg, USA) until the separation of the dolly from the specimens' surfaces occurred. Additionally, a proportion of cohesion failure in a substrate was estimated.

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RESULTS AND DISCUSSION

Relation between the gap distance and discharge appearance

As shown in Figure 2, the appearance of streamers is in good relation with early- and latewood distribution on the cross section of the treated sample. Darker regions of latewood (lower grey value) have a higher density and usually also exhibit a higher electrical conductivity. Therefore, the intensities of the discharge (higher grey values) are more pronounced in this regions.

It is also visible, that the distance between the insulated electrode and wood sample surface influenced the discharge density and plasma streamer distribution. At higher gap distances, the averaged grey values slightly decreased and the streamers were stronger localized, but seem to have higher energies as indicated by higher intensities.

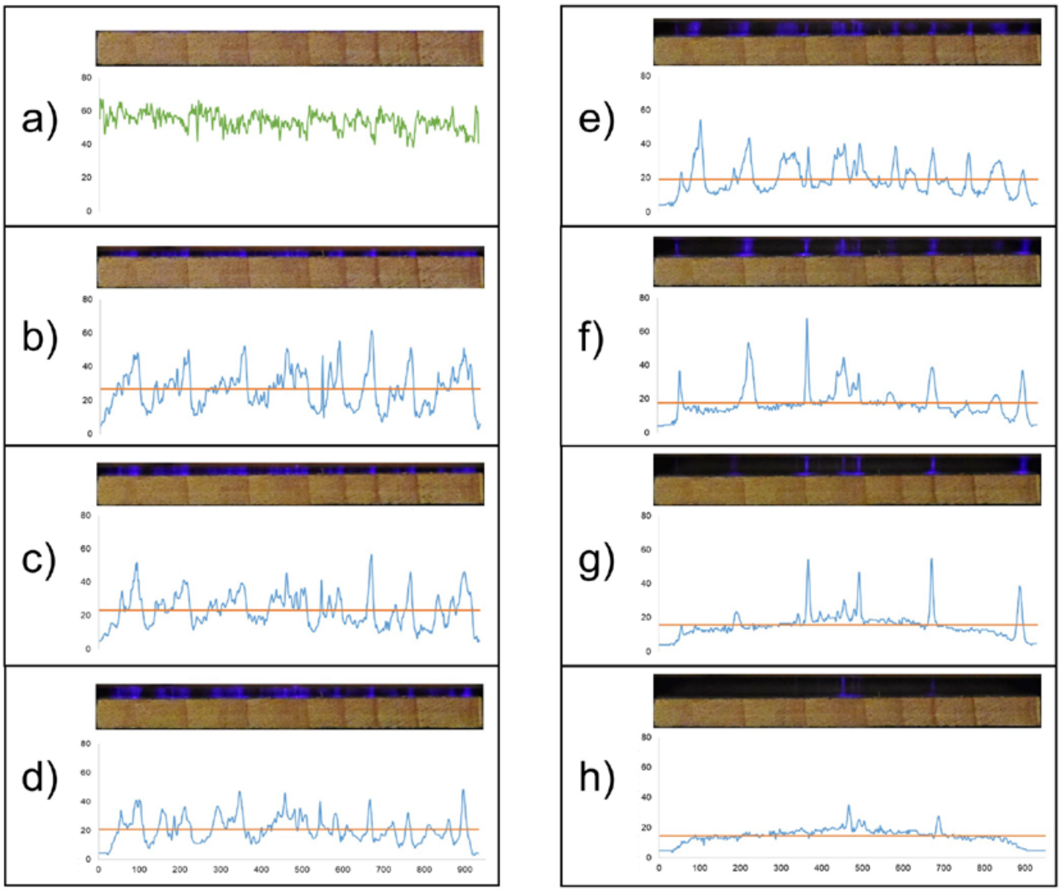

Fig. 2.
Distribution and intensity of the discharges [grey value/pixel] in dependence on beech wood sample structure and gap distance [mm]: a) wood sample cross section, b) 0.35, c) 0.40, d) 0.65, e) 1.00, f) 1.25, g) 1.45, h) 1.60.

Water droplet contact angle

The WCA decreased with increasing amount of NaCl on wood surfaces as depicted in Figure 3 and Figure 4. Additional PT made the substrates' surfaces even more hydrophilic. For both wood species, WCA were lower on non-impregnated PT surfaces than on impregnated surfaces without PT.

The lowest WCA were yielded on spruce wood modified with solution 7.2. On samples modified with the most concentrated NaCl solution, a less homogenous PT with streamers strongly localized on NaCl crystals might be the reason for slightly higher WCA.

On modified and PT beech wood surfaces, measured WCA were very low, because the droplets could be observed only few seconds after deposition. Therefore, the differences between the WCA on impregnated and PT beech wood surfaces are less well distinguishable.

Colour changes

The PT of control spruce and beech wood did not cause any changes to natural wood, which is in good agreement with other publications (Asandulesa *et al.* 2010; Žigon *et al.* 2019). However, after

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modification of samples with NaCl aqueous solutions, changes of colour, visible to the naked eye (*ΔE* ≥ 1), could be found for both spruce and beech wood (Figure 5). The increment of total difference of colour is correlated to the amount of NaCl present on the surfaces.

After PT, changes of surface colour became even more pronounced, again, in correlation with increased amount of NaCl present on the surface. Specimen modified with the two highest NaCl concentrations exhibited a number of burned spots after PT. This is a consequence of more localized electric fields at NaCl crystals, leading to partial carbonization of the main wood chemical components.

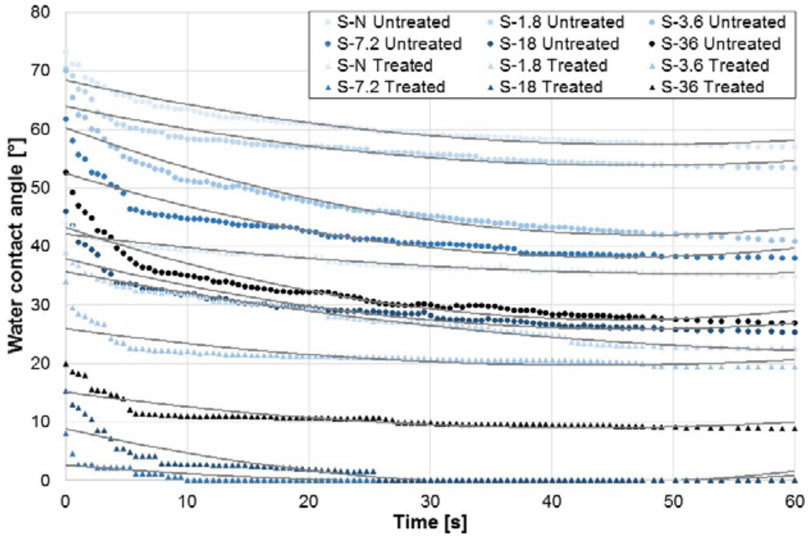

Fig. 2.
Contact angles of water droplets, deposited on normal, modified and treated spruce samples.

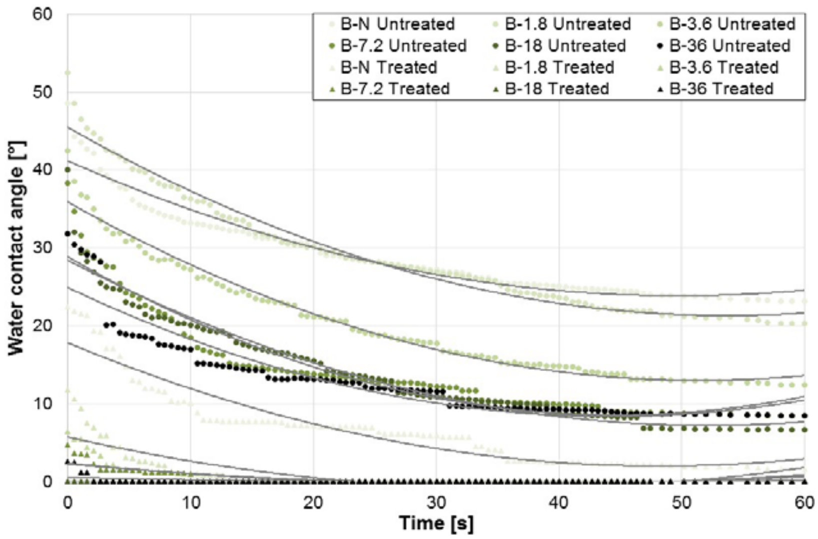

Fig. 3.
Contact angles of water droplets, deposited on normal, modified and treated beech samples.

SEM analysis of the coating systems and their adhesion strength

The adhesion pull-off strength of coating films on coated beech samples predominantly yielded adhesive-type fractures between substrate and coating film (Figure 6). Adhesion strength decreased with increasing amount of NaCl presented on the surface. The reason for that could be that crystals of NaCl poorly adhere to wood surface, presenting weakness spots in the interface between wood surface and coating film. Additionally, their presence on the wood surface might also hinder the penetration of the coating and therefore its sufficient mechanical anchoring. SEM micrographs of cross section beech samples, modified with the two highest NaCl concentrations are shown in Figure 7. For the highest NaCl concentration, salt crystals are visible in the wood-coating interface.

However, PT prior to coating application contributes to an increase of adhesion strength of the cured film in comparison to the corresponding untreated specimen.

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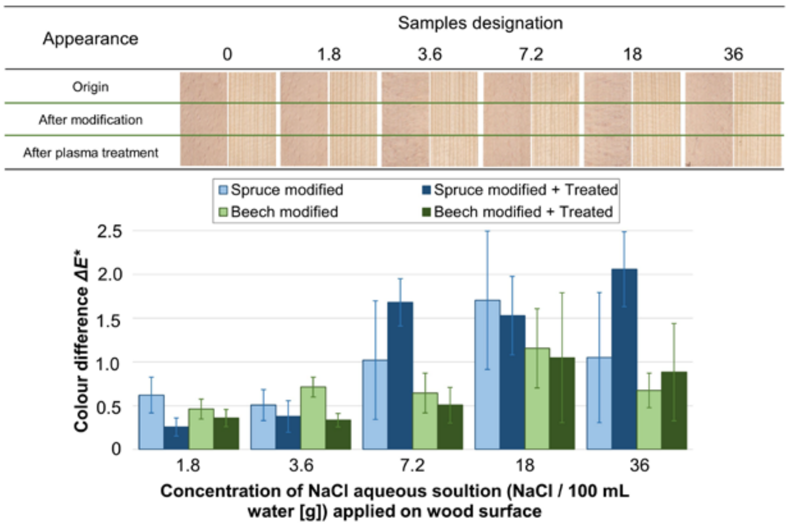

Fig. 5.
Colour difference of wood specimen due to impregnation and PT.

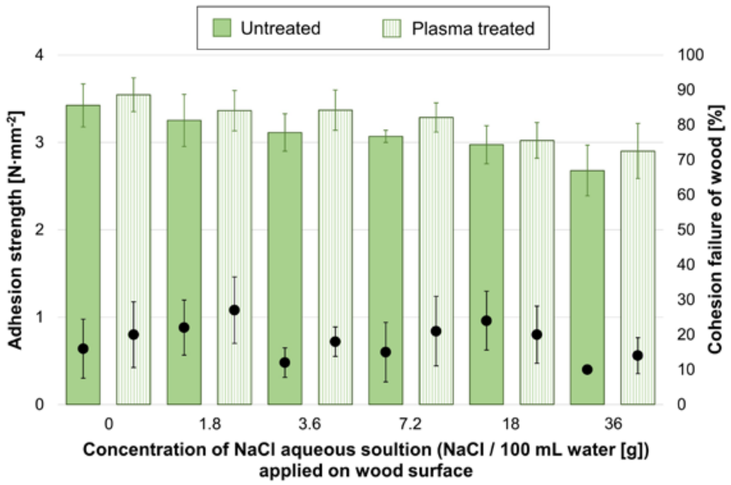

Fig. 6.
Coating system adhesion strength on percentage of cohesive failure of wood on normal, modified and PT beech wood.

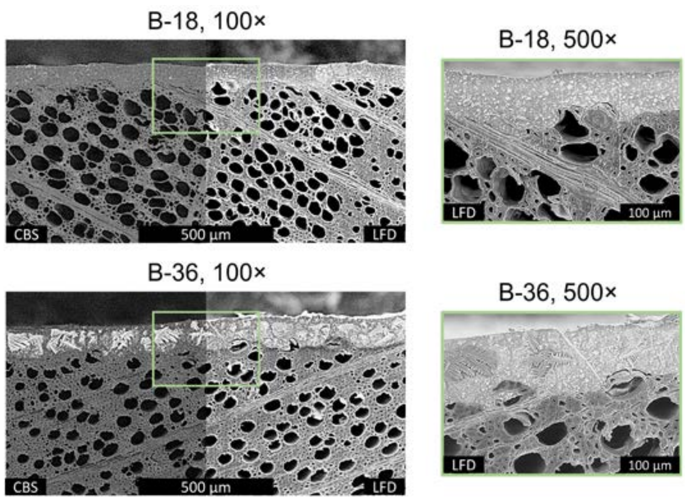

Fig. 7.
SEM micrograph of wood surface-coating interface on B-18 and B-36 sample, detected with CBS and LFD detector by different magnifications.

CONCLUSIONS

During the treatment of wood with DBD plasma, the shape and intensity of the discharge depends on the materials' electrical and dielectric properties. Intensities of the discharge are more pronounced and localized over latewood due to its higher density, electrical conductivity, and dielectric permittivity. This gets even more pronounced with increasing gap distance. Modification of spruce and beech wood surface with NaCl aqueous solutions made it more hydrophilic. Additional treatment with plasma additionally enhanced the wettability of modified surfaces with water. However, the NaCl impregnation has a negative impact on coating film adhesion strength. Further, high concentrations of NaCl and subsequent plasma treatment cause colour changes.

It was shown that introduction on Na and Cl ions into wood enhance the plasma treatment. Detailed experimental work is planned to be done to determine dielectric properties of such modified wood.

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