LES/WOOD Vol. 69, No. 2, 83-95
DOI: https://doi.org/10.26614/les-wood.2020.v69n02a03

PLASMA TREATMENT OF SPRUCE WOOD CHANGES ITS DIELECTRIC PROPERTIES

OBDELAVA SMREKOVEGA LESA S PLAZMO SPREMENI NJEGOVE DIELEKTRIČNE LASTNOSTI

Sebastian Dahle[1*], Jure Žigon[1], Marko Petrič[1], Mirko Kariž[1]

UDK 630*829.9:538.956
Original scientific article / Izvirni znanstveni članek

Received / Prispelo: 5. 10. 2020
Accepted / Sprejeto: 10. 11. 2020

Abstract / Izvleček

Abstract: *The effects of dielectric barrier discharge (DBD) plasma treatment on the dielectric properties of Norway spruce wood (*Picea abies *(L.) Karst.) were investigated using dielectric analysis. Dielectric constant (i.e. permittivity) and loss coefficient were determined at various frequencies. The resulting changes on lamellae specimens of different thicknesses were compared with the change in mass and moisture content. A significant influence of the plasma was found, leading to an increase of the dielectric constant by about 2%, and a decrease of sample mass directly after the plasma treatment by approx. 14%, whereas a reduction in moisture content by only about 0.6% and a corresponding change in loss coefficient were detected. Overall, the mechanisms of the observed changes remain unclear and seem mainly uncorrelated with the hitherto known chemical changes in wood surfaces caused by similar plasma discharges.*

Keywords: *wood, Norway spruce =* Picea abies*, plasma, dielectric constant, moisture content*

Izvleček: *Vpliv obdelave z dielektrično barierno razelektritveno (DBD) plazmo na dielektrične lastnosti smrekovega lesa (*Picea abies *(L.) Karst.) smo raziskovali z dielektrično analizo. Pri različnih frekvencah smo določili dielektrično konstanto in faktor dielektričnih izgub. Nastale spremembe na vzorcih lamel različnih debelin smo primerjali s spremembo mase in vlažnosti. Ugotovljen je bil pomemben vpliv obdelave s plazmo, kar je povzročilo povečanje dielektrične konstante za približno 2 % in zmanjšano maso vzorca neposredno po plazemski obdelavi, medtem ko je bilo zaznano zmanjšanje vlažnosti za približno 0,6 % in ustrezno povečanje tangensa izgubnega kota. Na splošno mehanizmi opaženih sprememb ostajajo nejasni in se zdijo v glavnem nepovezani z do zdaj znanimi kemičnimi spremembami na površinah lesa, ki jih povzročajo podobne plazemske razelektritve.*

Ključne besede: *les, navadna smreka =* Picea abies*, plazma, dielektrična konstanta, vlažnost*

1 INTRODUCTION

Plasma treatments are a good tool to modify the surface of wood-based materials and tailor them towards various applications, such as improving their compatibility with a given coating (Žigon et al., 2018; Altgen et al., 2019). The plasma has effects on the treated surfaces through various physical and chemical processes (Wolkenhauer et al., 2008; Altgen et al., 2015), thereby modifying the surface free energy (Blanchard et al., 2009), etching the surfaces (Jamali & Evans, 2011) or activating them (Žigon et al., 2019a). This also improves penetration and adhesion of the coatings, as well as the final properties of the formed surface system (Dam, 2017; Liston et al., 1993; Wolkenhauer et al., 2009; Wolf & Sparavigna, 2010; De Cademartori et al., 2016; Perisse et al., 2017; Reinprecht et al., 2018).

Král et al. (2015) found that the depth of the chemical modification by a non-thermal plasma is in the order of 100 nm inside the wood substrate. However, the depth of influence of plasma treatments might be deeper than shown by chemical modification of the solid material. Haase and co-workers (2019) found an etching of pits, which increased the substrates' porosity and thus enhanced the penetration of liquids applied after plasma treatment. Moreover, Wascher et al. (2014) proposed a possible treatment inside vessels, which changes the properties inside the material. This would include the overall effective or inner surface of the wood samples.

Non-thermal plasmas are capable of increasing the evaporation rates of liquids, including water

[1] University of Ljubljana, Biotechnical Faculty, Department of Wood Science and Technology, Jamnikarjeva 101, 1000 Ljubljana, Slovenia
[*] e-mail: sebastian.dahle@bf.uni–lj.si

(c.f. Gamaleev et al., 2019), which would affect the mechanical, electrical, and dielectric properties of a wooden specimen. This also applies to wooden workpieces, as previously shown on a wet beech substrate after 1 minute of localised DBD plasma treatment (Figure 1). The plasma-treated spot on the specimen's surface is significantly drier, and thus its colour stands out from the rest of the still wet surface.

The impact of plasma treatments for utilisation in gluing and coating applications is thus more complex than often assumed. Introducing a gradient of the moisture content will likely change the wetting, drying and curing of coatings and glues. Moreover, both, moisture content and dielectric properties are determining factors during most plasma treatments, which influence the electric fields and thus affect factors such as the transfer of energy, the gas temperatures, and the rates of plasma-chemical reactions.

The dielectric properties of a non-conducting material describe the interaction of the material with electric fields. The main interactions are the absorption and storage of electric potential energy in the form of polarisation within the dielectric material (dielectric constant ε', c.f. eq. 1), and the dissipation or loss of part of this energy when the electric field is removed (loss coefficient δ, aka loss tangent, c.f. eq. 2) (James, 1975). The dielectric constant is the ratio of the capacitance formed by two metal plates with a material between them, to the capacitance of the same plates with air (or a vacuum) between them.

$$\varepsilon = \varepsilon' - j\varepsilon'' \qquad (1)$$

$$tan\delta = \varepsilon'' / \varepsilon' \qquad (2)$$

In order to properly distinguish between electrical and dielectric properties, and to determine the frequency dependence, a combined inductance, capacitance and resistance (LCR) metre is used (Nikolova et al., 2018). Several factors affect the dielectric constant of wood, from the moisture content, density, and wood orientation (longitudinal, radial, tangential), to temperature and salinity (Torgovnikov, 1993; Sikder et al., 2009).

This is highlighted in Norimoto's 1976 overview on the dielectric properties of various wood

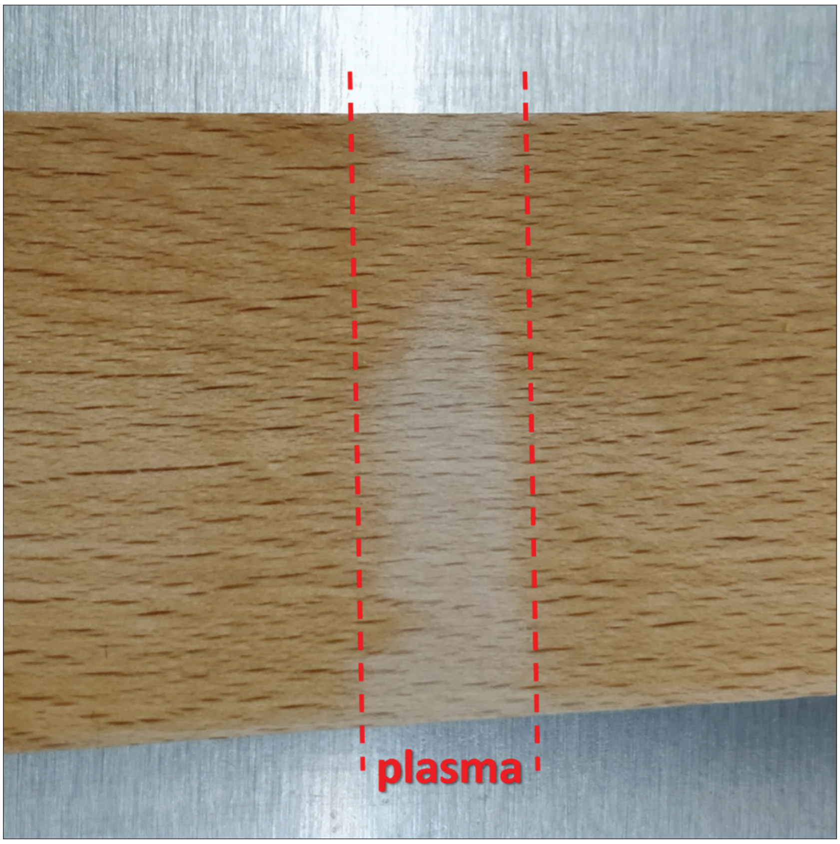

Figure 1. Wet beech substrate after 1 minute of localised DBD plasma treatment; the plasma-treated part of the surface (middle of the figure) standing out as being significantly drier than the rest of the specimen.

Slika 1. Moker substrat iz bukovine po 1 minuti lokalizirane obdelave z DBD plazmo; s plazmo obdelani del površine (sredina slike) izstopa kot bistveno bolj suh od preostalega vzorca.

species and lignocellulosic materials, and their dependence on temperature and moisture content. In relation to various microwave treatment and computer tomography applications, the local dielectric function inside the wood material is an important factor (c.f. Boero et al., 2018), giving rise to various models and generalised descriptions of the dielectric properties of wood (Daian et al., 2006).

In this study, we investigate the change in dielectric properties in spruce induced by an air plasma treatment. Further, mass and moisture content measurements are presented in order to discuss possible mechanisms. We hope to improve the understanding of these processes that determine the outcomes of plasma treatments for wood-based substrates.

1 UVOD

Obdelava s plazmo predstavlja dobro orodje za spreminjanje lastnosti površin materialov na osnovi lesa in njihovo prilagajanje različnim aplikacijam, npr. za izboljšanje njihove združljivosti s premazi (Žigon et al., 2018; Altgen et al., 2019). Plazma vpliva na obdelane površine s fizikalnimi in kemičnimi procesi na površinah obdelovancev (Wolkenhauer et al., 2008; Altgen et al., 2015), s čimer spreminja prosto energijo površin (Blanchard et al., 2009), jedka (Jamali & Evans, 2011) ali aktivira površine (Žigon et al., 2019a). To izboljša tudi prodiranje in oprijem premazov ter končne lastnosti površinskega sistema (Dam, 2017; Liston et al., 1993; Wolkenhauer et al., 2009; Wolf & Sparavigna, 2010; De Cademartori et al., 2016; Perisse et al., 2017; Reinprecht et al., 2018).

Král et al. (2015) so ugotovili globino kemijske modifikacije z netermično plazmo 100 nm znotraj lesnega substrata. Globina vpliva plazemske obdelave pa je lahko globlja kot pokaže kemijska analiza modifikacije trdnega materiala. Haase et al. (2019) so ugotovili jedkanje pikenjskih odprtin, kar je povečalo poroznost lesne strukture in s tem povečalo prodiranje tekočin, nanesenih po plazemski obdelavi.

Nadalje, Wascher et al. (2014) navajajo možno obdelavo znotraj celičnih lumnov in s tem spreminjanje lastnosti v poroznem materialu. To vključuje celotno specifično površino znotraj vzorcev lesa.

Netermične plazme povečajo hitrost izhlapevanja tekočin, vključno z vodo (Gamaleev et al., 2019), kar vpliva na mehanske, električne in dielektrične lastnosti lesnega vzorca. To pokaže tudi izpostavitev mokrega bukovega substrata lokalizirani obdelavi z DBD plazmo za 1 minuto (slika 1). Mesto na površini vzorca, obdelano s plazmo, je znatno osušeno, zato njegova barva izstopa v primerjavi s preostalo površino.

Vpliv plazemske obdelave na uporabo pri lepljenju in premazovanju je bolj zapleten, kot se pogosto domneva. Gradient vlažnosti bo verjetno spremenil omočitev, sušenje in utrjevanje premazov in lepil. Poleg tega sta vlažnost in dielektrične lastnosti odločilna dejavnika pri večini plazemskih obdelav, ki vplivajo na električna polja in tako vplivajo na prenos energije, temperaturo plinov in hitrosti plazemskih kemijskih reakcij.

Dielektrične lastnosti neprevodnega materiala opisujejo interakcijo materiala z električnimi polji. Glavni interakciji sta absorpcija in shranjevanje električne potencialne energije v obliki polarizacije znotraj dielektričnega materiala (dielektrična konstanta ε′, glej enačbo 1) in odvajanje ali izguba dela te energije ob odstranitvi električnega polja (faktor dielektričnih izgub δ, tudi tangens izgubnega kota, glej enačbo 2) (James, 1975). Dielektrična konstanta je razmerje med kapacitivnostjo, ki jo tvorita dve kovinski plošči z materialom med njima, in kapacitivnostjo enakih plošč z zrakom (ali vakuumom) med njima. Za pravilno razlikovanje med električnimi in dielektričnimi lastnostmi in za določitev frekvenčne odvisnosti se uporablja kombinirani merilnik induktivnosti, kapacitivnosti in upornosti (LCR) (Nikolova et al., 2018). Na dielektrično konstanto lesa vpliva več dejavnikov, kot so vlažnost, gostota, orientacija lesa (vzdolžno, radialno, tangencialno), temperatura in vsebnost soli (Torgovnikov, 1993; Sikder et al., 2009).

To je prikazano in razloženo v Norimotovem pregledu iz leta 1976 o dielektričnih lastnostih različnih vrst lesa in lignoceluloznih materialov ter njihovi odvisnosti od temperature in vsebnosti vlage. V zvezi z različnimi aplikacijami za mikrovalovno obdelavo in računalniško tomografijo je lokalna dielektrična funkcija znotraj lesnega materiala pomemben dejavnik (Boero et al., 2018), kar je povzročilo razvoj različnih modelov in opisov dielektričnih lastnosti lesa (Daian et al., 2006).

V tej študiji smo raziskovali spremembe dielektričnih lastnosti lesa smreke, ki jih povzroči obdelava z zračno plazmo. Nadalje so predstavljene meritve mase in vlažnosti z namenom razprave o možnih mehanizmih. Na ta način bi lahko izboljšali razumevanje procesov, ki določajo rezultate plazemske obdelave lesnih substratov.

2 MATERIALS AND METHODS
2 MATERIALI IN METODE

2.1 PLASMA TREATMENT PROCESS

The surface of each individual sample was treated with a dielectric barrier discharge (DBD) device (also known as a direct Cold Atmospheric Plasma, diCAP) that generates a non–thermal plasma in air at atmospheric pressure (Rehn & Viöl, 2003; Altgen et al., 2016; Žigon et al., 2019b) in a setup as depicted in Figure 2. The parameters of an alternating high voltage (frequency 5 kHz, 15 kV peak voltage) were regulated via a high voltage generator (c.f. Žigon et al., 2019a, b). Plasma was ignited between the surface of the treated specimen (moving rate 3 mm·s^{-1}) and a tubular ceramic hose (Al_2O_3, thickness 2.5 mm) with a round brass electrode with a diameter of 15 mm. The distance between the dielectric and the surface of the specimen was set to 1 mm. All samples were treated individually to reduce holding times between treatment and subsequent measurements.

2.1 POSTOPEK OBDELAVE S PLAZMO

Površina vsakega posameznega vzorca je bila obdelana z dielektrično barierno razelektritveno plazmo (DBD) (znano tudi kot neposredna hladna atmosferska plazma, diCAP), ki v zraku ustvarja netermično plazmo pri atmosferskem tlaku (Rehn & Viöl, 2003; Altgen et al., 2016; Žigon et al., 2019b) in katere shema je prikazana na sliki 2. Parametri izmenične visoke napetosti (frekvenca 5 kHz, 15 kV najvišja napetost) so bili regulirani prek visokonapetostnega generatorja (Žigon et al., 2019a, b). Plazma se je ustvarila med površino obdelovanca (hitrost gibanja 3 mm s^{-1}) in keramično cevjo (Al_2O_3, debelina 2,5 mm) z okroglo medeninasto elektrodo s premerom 15 mm v notranjosti. Razdalja med dielektrikom in površino obdelovanca je bila nastavljena na 1 mm. Vse vzorce smo obdelali posamično, da smo skrajšali čas med obdelavo in naslednjimi meritvami.

2.2 DIELECTRIC MEASUREMENTS

Dielectric analysis (DEA) involves measuring changes of the dielectric properties of the material by using an impedance analyser over many orders of magnitude of frequency. Dielectric measurements are carried out by measuring the voltage and current between a pair of electrodes in order to determine the conductance and capacitance of the material placed between the electrodes (Šernek & Kamke, 2007). From these measurements the dielectric constant and loss coefficient can be determined.

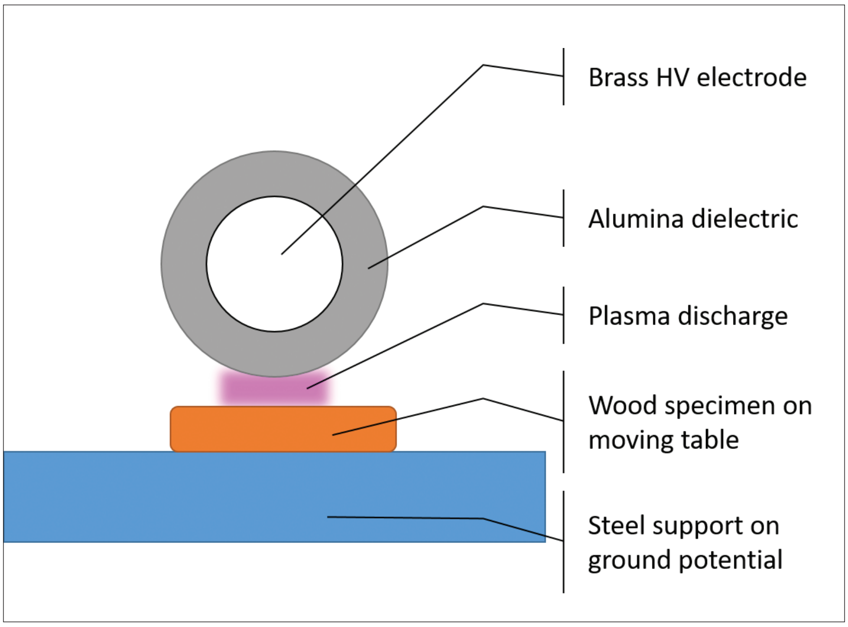

Figure 2. Schematic representation of the used plasma setup.
Slika 2. Shematski prikaz uporabljene naprave s plazmo.

Radial cut lamellas with thicknesses of 3 mm and 5 mm were cut with a laser from spruce (*Picea abies* (L.) Karst.), producing five wooden discs for each thickness, each with a diameter of 55 mm. Discs edges were sanded to remove the charred material, which could affect the measurements. The residual moisture content of the discs amounted to approx. 9.4%.

The wooden discs were weighed before measuring the initial dielectric properties, immediately after conducting the plasma treatment described in 2.1, and before each measuring of the dielectric properties. Dielectric measurements were conducted immediately after plasma treatment and 24 and 48 hours after.

Measurements of dielectric properties were carried out at room temperature using an Agilent 4285A LCR metre together with an Agilent 16451B Dielectric Test Fixture. The dielectric properties were determined within a frequency range of 79 kHz to 25 MHz. A measuring method with an air gap of 1 mm between the upper electrode and samples was used to measure the dielectric properties without the influence of the samples' conductivity.

The resulting data were averaged from measurements of all equal samples before determining the dielectric constant and loss coefficient of wood, following Šernek and Kamke (2007).

2.2 DIELEKTRIČNE MERITVE

Dielektrična analiza (DEA) vključuje merjenje sprememb dielektričnih lastnosti materiala pri različnih frekvencah z uporabo impedančnega analizatorja. Dielektrične meritve se izvajajo z merjenjem napetosti in toka med parom elektrod, s čimer se ugotovi prevodnost in kapacitivnost materiala, nameščenega med elektrodama (Šernek & Kamke, 2007). Iz teh meritev lahko določimo dielektrično konstanto in faktor dielektričnih izgub.

Iz vsake smrekove (*Picea abies* (L.) Karst.) lamele debelin 3 in 5 mm z radialno orientacijo lesnih vlaken smo z laserjem izrezali po pet lesenih diskov s premerom 55 mm. Robove diskov smo pobrusili, da smo odstranili zogleneli material, ki bi lahko vplival na meritve. Vlažnost diskov je bila približno 9,4 %.

Lesene diske smo stehtali pred začetnim merjenjem dielektričnih lastnosti, tik po obdelavi s plazmo (postopek opisan v točki 2.1) ter pred vsakim merjenjem dielektričnih lastnosti. Dielektrične lastnosti smo merili takoj po obdelavi s plazmo ter po 24 in 48 urah po obdelavi.

Meritve dielektričnih lastnosti smo izvedli pri sobni temperaturi z uporabo merilnika LCR Agilent 4285A skupaj z napravo za merjenje dielektričnih lastnosti trdih snovi Agilent 16451B. Dielektrične lastnosti so bile določene v frekvenčnem območju od 79 kHz do 25 MHz. Za merjenje dielektričnih lastnosti brez vpliva prevodnosti vzorcev je bila uporabljena metoda z zračno režo 1 mm med zgornjo elektrodo in vzorcem.

Nastali podatki so bili iz meritev vseh enakih vzorcev povprečeni pred določitvijo dielektrične konstante in tangensa izgubnega kota lesa na način, kot sta ga opisala Šernek in Kamke (2007).

2.3 MOISTURE CONTENT AND MASS CHANGE

The impact of the plasma treatment on the moisture content and mass change coinciding with that were determined on spruce radial cut lamellas sized 50 mm × 35 mm × 3.1 mm. Moisture contents were measured using a Gann Hydromette M 4050 with a ram-in electrode M18, set to the manufacturer's parameters for spruce wood. The mass change during plasma treatments were measured using a Mettler Toledo PB1502 scale. Video recordings of the treatment showing the sample and the display of the scale were analysed frame by frame to yield two values per second (full recording available together with all the raw data).

2.3 SPREMEMBA VSEBNOSTI VLAGE IN MASE

Vpliv obdelave s plazmo na vlažnost in sorazmerno spremembo mase smo določili na smrekovih radialno rezanih lamelah velikosti 50 mm × 35 mm × 3,1 mm. Lesno vlažnost smo izmerili z vlagomerom Gann Hydromette M 4050 z vstavljeno elektrodo M18, nastavljeno na proizvajalčeve parametre za smrekov les. Sprememba mase med obdelavo s plazmo je bila izmerjena s tehtnico Mettler Toledo PB1502. Iz posnetkov obdelave s plazmo, ki prikazujejo vzorce in merilo, smo zajeli po dve meritvi vrednosti na sekundo (na voljo celotno snemanje skupaj z vsemi neobdelanimi podatki).

3 RESULTS AND DISCUSSION

In Figure 3, the dielectric properties in the range from 0 to 25 MHz for spruce disks with a thickness of 3 mm are shown before plasma treatment (blue line), directly after plasma treatment (pink line), 24 hours after plasma treatment (grey line) and 48 hours after plasma treatment (yellow line). Directly after the plasma treatment, the dielectric constant was increased by about 2%, which is contrary to expectations with regard to drying processes. As the moisture content decreases and volatile organic compounds evaporate from the specimen the dielectric constant should decrease, because of the higher dielectric constant of the evaporated compounds as compared to the residual material (c.f. Norimoto & Yamada, 1972; James, 1975; Torgovnikov, 1993). The effect does remediate over time, as can be clearly seen from measurements after 24 and 48 hours. However, the remediation appears to differ over the frequency range, being particularly faster in the range above 20 MHz, whereas a larger dielectric constant is retained particularly below 5 MHz, even after 48 hours.

Based on the measured change in dielectric constant, it is possible to try and estimate the depth of the effect imposed by the plasma treatment by assuming distinct values of the base dielectric constant ε_1 over a thickness of d_1 inside the sample, as well as a dielectric constant ε_2 in a layer of thickness d_2, which was changed by the plasma within no more than one order of magnitude. The setup is effectively represented by a serious of planar capacitors with cross-sectional area A of capacitance C (see eq. 3), yielding a total external capacitance of C_{tot} (see eq. 4).

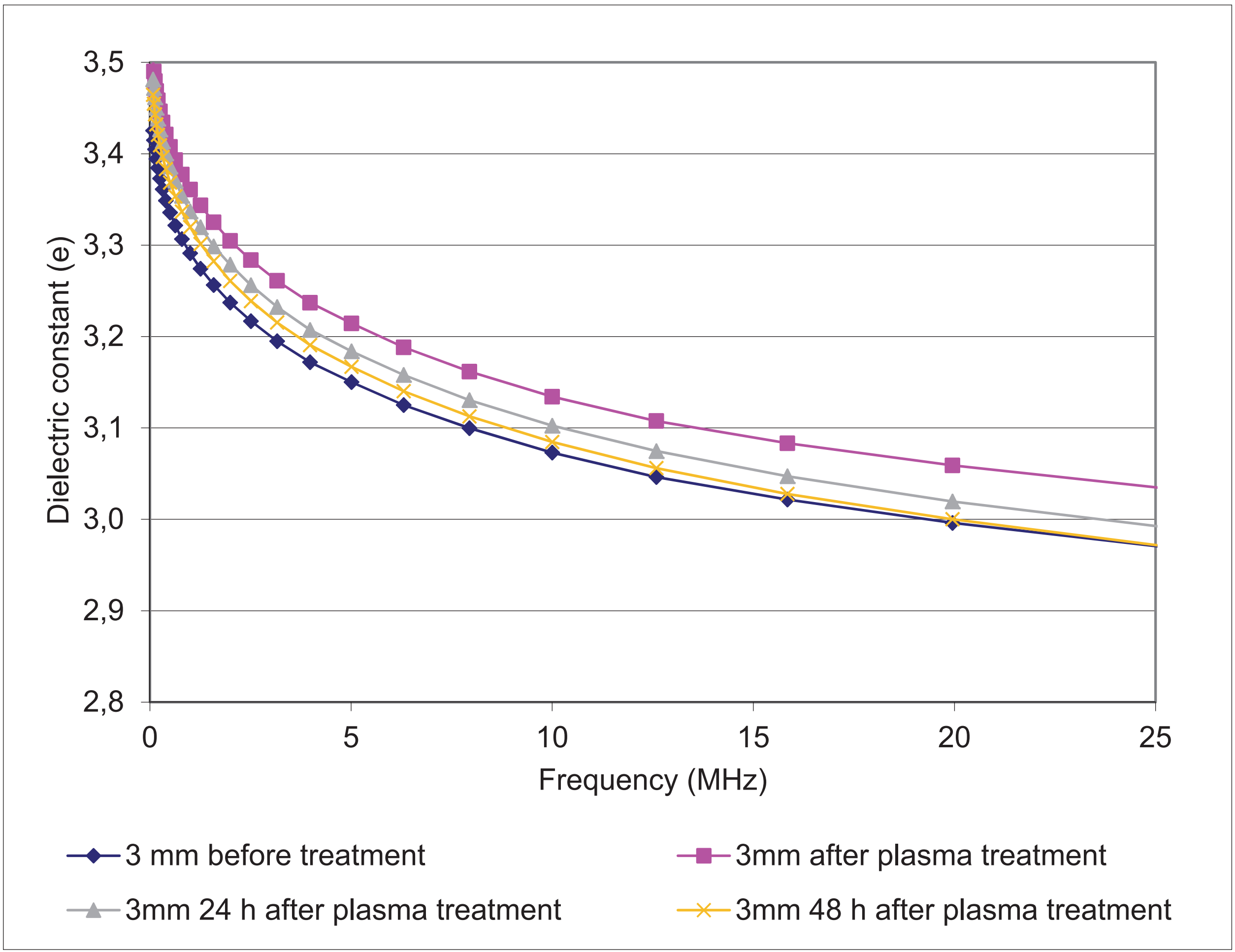

Figure 3. Dielectric constant of spruce discs, thickness 3 mm

Slika 3. Dielektrična konstanta smrekovih diskov debeline 3 mm

$$C = \varepsilon A / d \quad (3)$$

$$C_{tot}^{-1} = C_1^{-1} + C_2^{-1} \quad (4)$$

Simple transformations of equations 3 and 4 for an initial dielectric constant ε, a measured change by 2% and a maximum local change of a factor of 10, yield the relative thicknesses of the unmodified bulk d_{bulk} and the modified layer d_{mod} as given by eq. 5, which can be simplified into eq. 6. This amounts to a modified layer thickness d_{mod} of 2.2% of the remaining unmodified bulk d_{bulk}, i.e. 66 µm modification depth within the 3 mm lamellae. It should be noted that these figures overestimate typical changes in the dielectric constant imposed by chemical modifications in wood, thus likely underestimating the actual modification depth by a significant factor.

Figure 4 shows measurements of the dielectric constant in the range from 0 to 25 MHz for spruce disks with a thickness of 5 mm. Data are shown for the specimen before plasma treatment (blue line), directly after plasma treatment (pink line), 24 hours after plasma treatment (grey line), and 48 hours after plasma treatment (yellow line). In contrast to the 3 mm disks, the volume dielectric constant for the 5 mm disks does not show a significant change due to the plasma treatment, but a slight decrease in the region above 20 MHz is notable 24 hour after the treatment. This difference between 3 mm and 5 mm thick disks indicates the limited depth of the plasma treatment's effect. Since the effect is still well pronounced with the integrated dielectric properties of 3 mm thick specimens, but barely visible at all at 5 mm thick specimens, the impact

$$(d_{bulk} + d_{mod}) / (1.02 \cdot \varepsilon) = [\, d_{bulk} / \varepsilon \,] + [\, d_{mod} / (10 \cdot \varepsilon) \,] \quad (5)$$

$$d_{mod} = [\, 0.2 / 8.98 \,] \cdot d_{bulk} \quad (6)$$

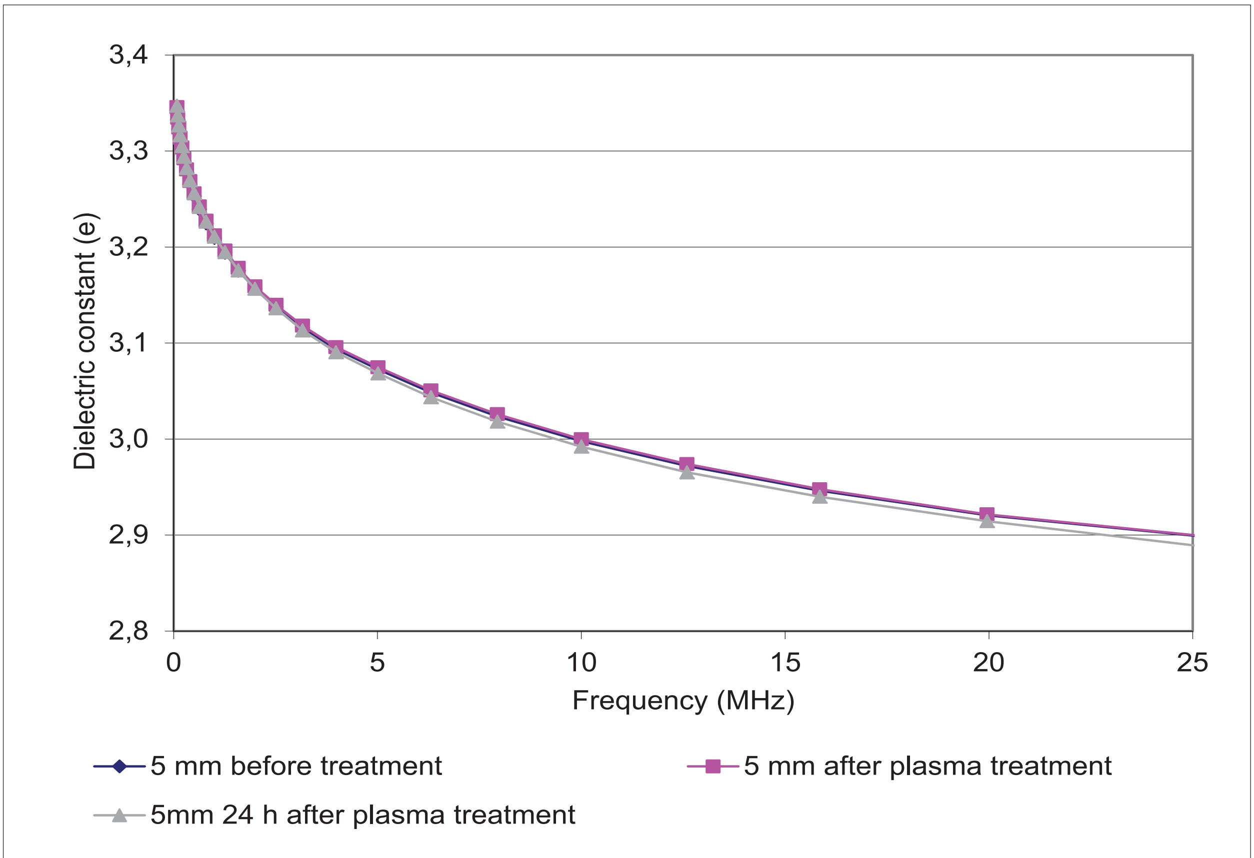

Figure 4. Dielectric constant of spruce discs, thickness 5 mm

Slika 4. Dielektrična konstanta smrekovih diskov debeline 5 mm of the plasma treatment on the dielectric properties seems to be in the area near the surface. The method used for measuring dielectric properties shows the average dielectric constant through the sample.

Figure 5 presents the loss coefficients for 3 mm spruce discs before plasma treatment (blue line), directly after plasma treatment (pink line) and 24 hours after plasma treatment (grey line). The lowest loss coefficients in the entire frequency range are represented by the untreated substrates; however, the increase in losses appears insignificant against natural variations of the material. The changes in dielectric permittivity (c.f. fig. 3) are thus not reflected in an increased absorption of energy out of alternating electrical fields. Since both the dielectric permittivity and the loss coefficient are typically most effected by changing moisture contents at frequencies below 100 kHz, the loss coefficient even more so than the dielectric constant (c.f. James, 1975), it seems unlikely that these effects are caused merely by an enhanced evaporation of volatile compounds from the surface, which is known to appear during plasma treatments (Altgen et al., 2015, 2016).

In order to investigate possible causes for the changes in dielectric constant and loss coefficient, the mass change of a 50 mm × 35 mm × 3.1 mm spruce lamella was observed throughout and after the plasma treatment process. An evaluation of the mass change over 120 s after being exposed to plasma relative to the weight before the plasma treatment is given in the dataset (see supplemental material and raw data).

Figure 6 shows a comparison between the mass and corresponding moisture content of a specimen before and after plasma treatment, as well as the relative change of both properties. The effect of

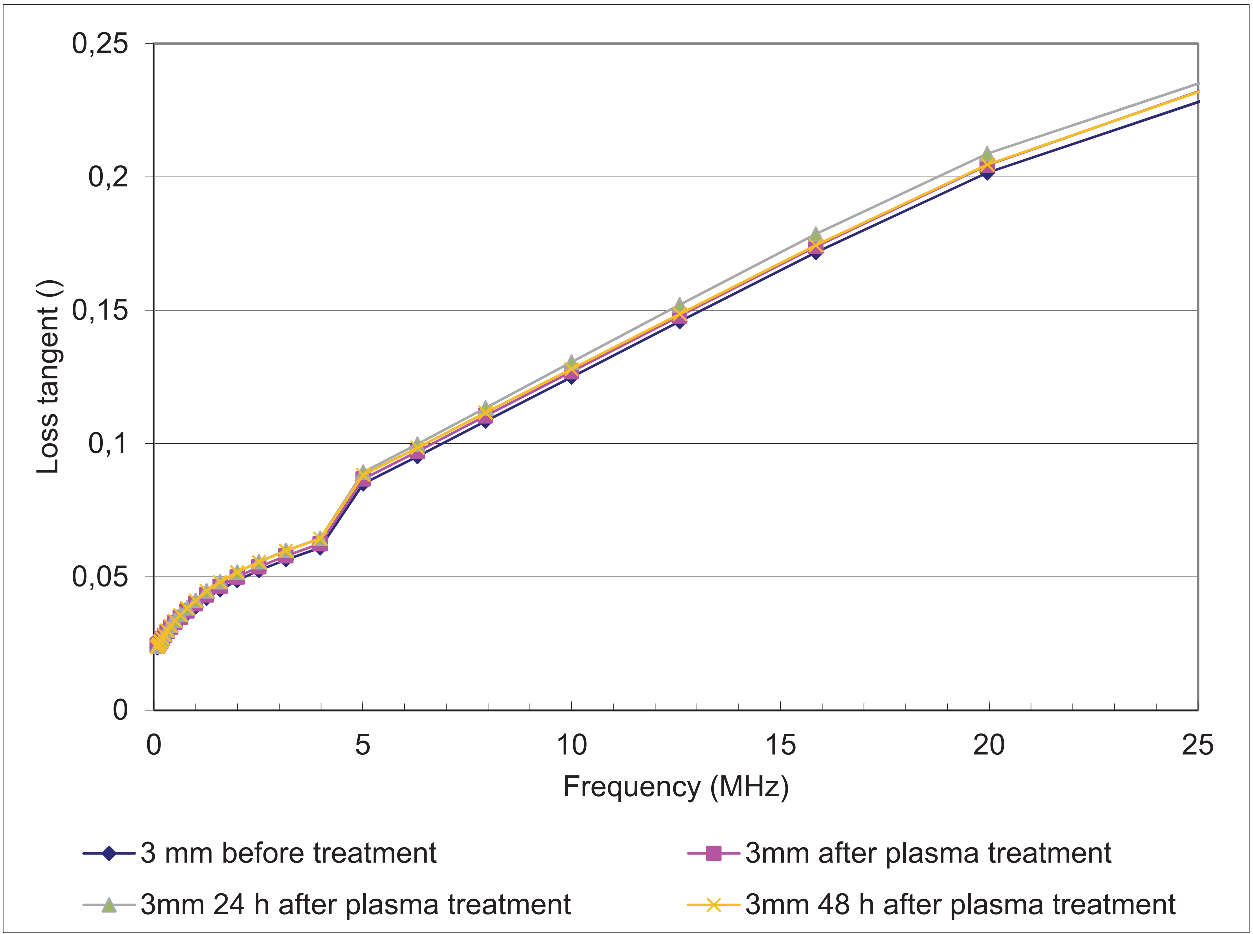

Figure 5. Loss coefficient of spruce discs, thickness 3 mm
Slika 5. Faktor dielektričnih izgub smrekovih diskov debeline 3 mm

enhanced evaporation, removal of small volatile organic compounds and the decrease of moisture content within the part of the wood near the surface is known in the literature (c.f. Altgen et al., 2015, 2016), and the measured moisture reduction of 0.6% correlates well with current knowledge. However, a monitoring of the weight throughout the plasma treatment revealed a stronger reduction than expected. During the plasma treatment, electrostatic interactions rendered the measured weights invalid; the differential weights shown in fig. 6 were thus taken only after the specimen had been removed from the gap underneath the plasma electrode. The strongly reduced weight after the plasma treatment, amounting to approx. 86% of the initial weight slowly rose again over two minutes to approx. 88% of the initial weight. Despite strong variations (due to the airflow in the laboratory), the tendency is clearly visible and the extent of the physical weight loss well exceeds all expectations from measurements on changes in chemical composition from earlier publications. A further investigation the impact of plasma on wood samples in terms of weight change would be worthwhile to better understand the underlying processes and improve the statistics of the measurements.

The influence of plasma treatments on the chemistry of wood substrates is typically considered to be on the order of magnitude of 1 µm (Král et al., 2015). However, it has been suggested that the plasma might be ignited somewhat deeper in the wood material (Wascher et al., 2014), which is

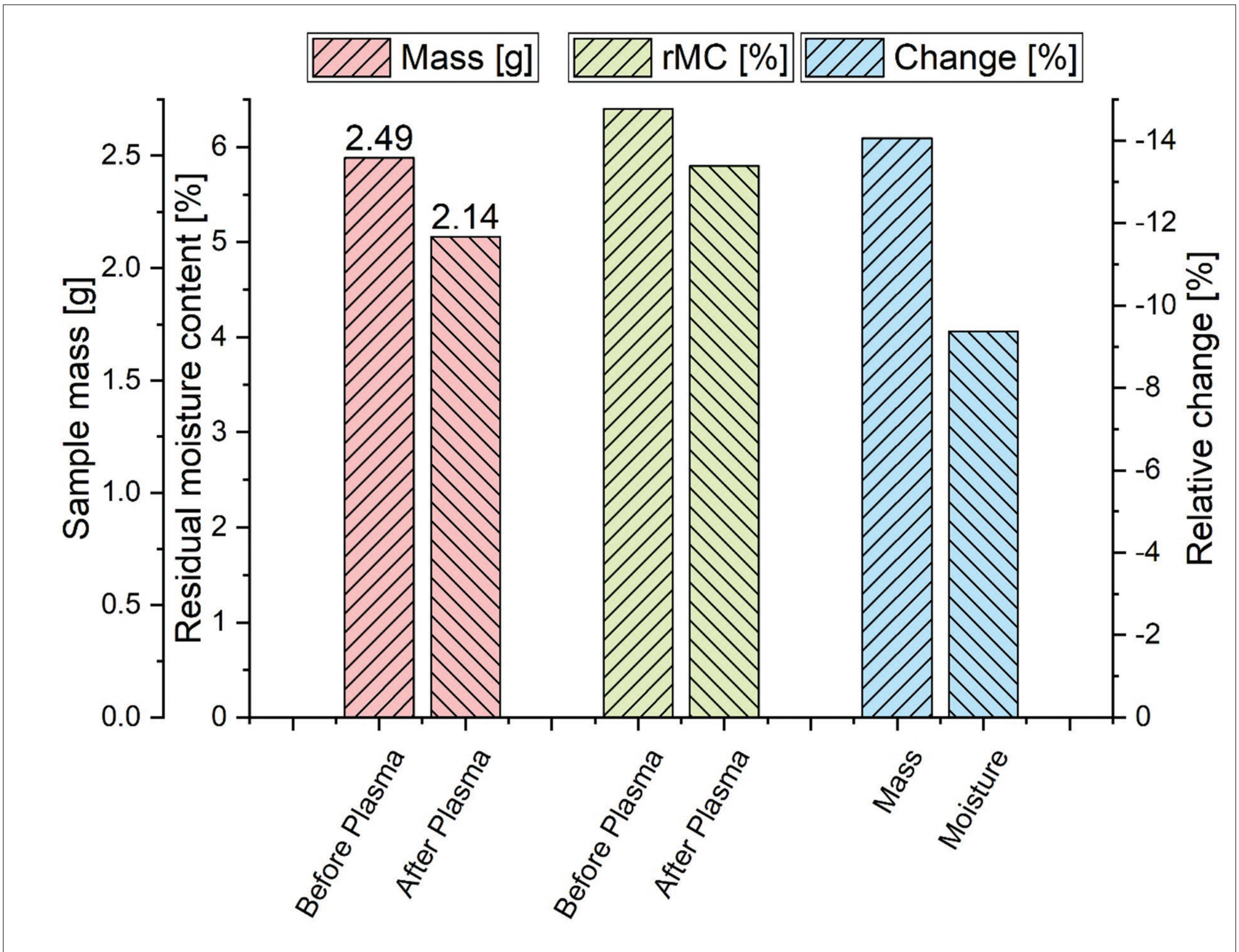

Figure 6. Mass and residual moisture content (rMC) of a spruce lamella with a thickness of 3 mm before and after plasma treatment, as well as the relative changes of mass and rMC

Slika 6. Masa in vlažnost smrekove lamele debeline 3 mm pred obdelavo s plazmo in po njej ter relativne spremembe mase in vlažnosti.

in line with the measured change in moisture content. Moreover, the observed change in dielectric permittivity, particularly for the 3 mm thick lamellae, clearly requires a deeper influence throughout a large part of the specimen, which corresponds well to the observed weight loss after plasma treatment. From both the known chemical effects and the measured change in moisture content, it is clear that the weight loss and change in dielectric permittivity must include other driving mechanisms. This deduction is further supported by the frequency-dependent change in dielectric parameter and the change in dielectric loss coefficient relative to this. It is worth noting, however, that residual charge might still have a minor influence on the measured weight, and that the absolute values of residual moisture content (rMC), as measured via an electric moisture metre, do differ from the average 9.4 % rMC determined through mass change during oven drying. Therefore, further studies are required to illuminate the processes causing these observations.

3 REZULTATI IN RAZPRAVA

Na sliki 3 so prikazane dielektrične lastnosti v območju meritev od 0 do 25 MHz za smrekove diske debeline 3 mm pred obdelavo s plazmo (modra krivulja), neposredno po obdelavi s plazmo (rožnata krivulja), 24 ur po obdelavi s plazmo (siva krivulja) in 48 ur po obdelavi s plazmo (rumena krivulja). Neposredno po obdelavi s plazmo se je dielektrična konstanta povečala za približno 2 %, kar je v nasprotju s pričakovanji v povezavi s sušenjem. Ko se vlažnost lesa zmanjšuje in hlapne organske spojine iz vzorca izhlapijo, se mora zmanjšati tudi dielektrična konstanta zaradi večje dielektrične konstante uparjenih spojin v primerjavi s preostalim materialom (Norimoto & Yamada, 1972; James, 1975; Torgovnikov, 1993). Učinek se sčasoma zmanjša, kot je razvidno iz meritev po 24 in 48 urah. Vendar se zdi, da se znižanje razlikuje glede na frekvenco meritve, saj je hitrejše v območju nad 20 MHz, medtem ko se večja dielektrična konstanta še ohranja pod 5 MHz.

Na podlagi izmerjene spremembe dielektrične konstante je mogoče poskusiti oceniti globino učinka, ki ga povzroči plazemska obdelava, tako da predpostavimo različne vrednosti osnovne dielektrične konstante ε_1 pri debelini sloja d_1 znotraj vzorca in dielektrične konstante ε_2 v plasti debeline d_2, ki jo je plazma spremenila za največ 1-kratnik vrednosti. Princip lahko učinkovito predstavimo z zaporedjem ploščatih kondenzatorjev s prerezom A in kapacitivnostjo *C* (glej enačbo 3), kar daje skupno zunanjo kapacitivnost C_{tot} (glej enačbo 4).

Preproste transformacije enačb 3 in 4 za začetno dielektrično konstanto ε pred obdelavo s plazmo, izmerjena sprememba dielektrične konstante za 2% in največja lokalna sprememba za faktor 10 dajejo relativno debelino nespremenjenega materiala d_{bulk} in spremenjene plasti d_{mod}, kot je podano z enačbo 5, ki jo je mogoče poenostaviti v enačbo 6. Od tod se lahko izračuna spremenjeno debelino plasti d_{mod}, ki znaša 2,2 % materiala, kar absolutno pomeni globino modifikacije 66 µm v 3 mm debelih lamelah. Opozoriti je treba, da je ta ocena pretirana glede na tipične spremembe dielektrične konstante, ki izhajajo iz pričakovanih kemičnih sprememb v lesu, in tako verjetno podcenjujejo dejansko globino modifikacije.

Slika 4 prikazuje meritve dielektrične konstante v območju od 0 do 25 MHz za smrekove diske debeline 5 mm. Podatki so prikazani za vzorec pred obdelavo s plazmo (modra krivulja), neposredno po obdelavi s plazmo (rožnata krivulja), 24 ur po obdelavi s plazmo (siva krivulja) in 48 ur po obdelavi s plazmo (rumena krivulja). V nasprotju z diski debeline 3 mm dielektrična konstanta diskov z debelino 5 mm ne kaže bistvene spremembe zaradi obdelave s plazmo, le rahlo zmanjšanje v območju nad 20 MHz je opazno 24 ur po obdelavi s plazmo. To kaže na omejeno globino učinka plazemske obdelave, ki je vedno dobro izražena s spremenjenimi dielektričnimi lastnostmi vzorcev debeline 3 mm, vendar pri vzorcih debeline 5 mm komaj vidna. Uporabljena metoda merjenja dielektrične vrednosti namreč meri povprečno vrednost na merjenem vzorcu.

Slika 5 prikazuje faktor dielektričnih izgub za smrekove diske debeline 3 mm pred obdelavo s plazmo (modra krivulja), neposredno po obdelavi s plazmo (rožnata krivulja), 24 ur po obdelavi s plazmo (siva krivulja) in 48 ur po obdelavi s plazmo (rumena krivulja). Najnižji faktor dielektričnih izgub v celotnem frekvenčnem območju je bil zaznan pri neobdelanih preizkušancih, povečanje izgub pa se zdi neznačilno glede na naravno variabilnost lesa. Spremembe dielektrične konstante (glej sliko 3) se tako ne odražajo v povečani absorpciji energije iz izmeničnih električnih polj. Ker na dielektričnost in faktor dielektričnih izgub običajno največ vpliva spreminjanje vlažnosti lesa pri frekvencah pod 100 kHz, na faktor dielektričnih izgub celo bolj kot na dielektrično konstanto (James, 1975), se ne zdi zelo verjetno, da so ti učinki posledica zgolj povečanega izhlapevanja hlapnih spojin s površine, za katero je znano, da se pojavi med obdelavo s plazmo (Altgen et al., 2015, 2016).

Da bi raziskali možne vzroke za spremembo dielektrične konstante in faktorja dielektričnih izgub, je bila sprememba mase smrekove lamele 50 mm × 35 mm × 3,1 mm izmerjena med postopkom plazemske obdelave in po njej. V naboru podatkov je podana ocena spremembe mase v 120 s po izpostavitvi plazmi glede na maso pred obdelavo s plazmo (prikazano v dodatnih neobdelanih podatkih).

Slika 6 prikazuje primerjavo mase smrekove lamele in njene ustrezne vsebnosti vlage v vzorcu pred in po obdelavi s plazmo ter relativno spremembo obeh lastnosti. Vpliv povečanega izhlapevanja, odstranjevanja majhnih hlapnih organskih spojin in padanja vlažnosti v površinskem delu lesa je znan v literaturi (prim. Altgen et al., 2015, 2016), izmerjeno zmanjšanje za 0,6 % pa pričakovano. Vendar je spremljanje spremembe mase s plazemsko obdelavo pokazalo močnejše zmanjšanje, kot je bilo pričakovano. Med obdelavo s plazmo so elektrostatske interakcije povzročile, da so bile izmerjene mase nepravilne, zato so na sliki 6 prikazane meritve od trenutka, ko se vzorec odstrani iz reže pod plazemsko elektrodo. Močno zmanjšana masa po plazemski obdelavi (približno 86 % začetne mase) se je v dveh minutah počasi spet dvignila na približno 88 % začetne mase. Kljub velikim nihanjem v meritvah mase (zaradi gibanja zraka v laboratoriju z vzgonskimi učinki) je tendenca jasno vidna in obseg izgube mase močno presega vsa pričakovanja glede na navedene spremembe kemijske sestave iz prej omenjenih publikacij. Potrebno je nadaljevanje raziskovanja vpliva plazme na vzorce lesa glede na spreminjanje njihove mase, da bi bolje razumeli osnovne procese in izboljšali zanesljivost meritev.

Vpliv obdelave s plazmo na kemijske lastnosti lesnega substrata je zabeležen do globine reda velikosti 1 µm (Král et al., 2015). Poleg tega smo predvidevali, da se plazma lahko pojavi tudi nekoliko globlje znotraj lesenega materiala, npr. v odprtih porah (Wascher et al., 2014). To potrjuje tudi razmeroma močno spremenjena izmerjena vlažnost lesa in govori o globini učinka bistveno pod 1 µm debelim površinskim slojem, čeprav tega v predhodnih raziskavah s FTIR spektroskopijo ni bilo mogoče potrditi. Vpliv plazme na opaženo spremembo dielektrične konstante pa je očiten zlasti pri 3 mm debelih lamelah, kar dobro ustreza ugotovljeni izgubi mase po obdelavi s plazmo. Iz znanih kemijskih učinkov in izmerjene spremembe vlažnosti lesa je razvidno, da morata izguba mase in sprememba dielektričnih lastnosti vključevati tudi druge vzroke. Takšno sklepanje je podprto s frekvenčno odvisno spremembo dielektričnih parametrov in relativno spremembo tangensa izgubnega kota. Vendar je treba omeniti, da bi lahko imeli morebiti preostali električni naboji še vedno manjši vpliv na izmerjeno težo ter da se absolutne vrednosti vlažnosti, izmerjene z električnim merilnikom vlage, razlikujejo od povprečnih 9,4 % vlažnosti, določenih s spremembo mase med sušenjem v sušilniku. Za razjasnitev teh procesov in opazovanj pa so potrebne nadaljnje študije.

4 SUMMARY

- Distinct rise in dielectric permittivity after plasma treatment, particularly on thinner lamellae and towards higher frequencies well above 1 MHz, but negligible change of loss coefficient.
- Minor reduction of residual moisture content, but strong weight reduction in plasma-treated wood lamella.
- Dielectric properties are affected by plasma treatment much deeper within the bulk material than has previously been reported for the maximum depth of chemical modifications by plasma treatments.

4 POVZETEK

- Izrazit dvig dielektrične konstante po obdelavi s plazmo, zlasti pri tanjših vzorcih in višjih frekvencah precej nad 1 MHz, vendar zanemarljiva sprememba tangensa izgubnega kota.
- Majhno zmanjšanje lesne vlažnosti, vendar močno zmanjšanje mase pri leseni lameli, obdelani s plazmo.
- Obdelava s plazmo vpliva na dielektrične lastnosti veliko globlje v materialu, kot so doslej poročali glede največje globine kemičnih modifikacij pri obdelavi lesa s plazmo.

Acknowledgements:

The authors acknowledge the provision of the moisture meter by the group of Prof. Dr. Ž. Gorišek.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 745936.

The authors acknowledge further financial support from the Slovenian Research Agency (research program funding No. P4–0015, "Wood and lignocellulosic composites").

Zahvala:

Avtorji se zahvaljujemo skupini prof. dr. Ž. Goriška, da je omogočila uporabo merilnika lesne vlažnosti.

Ta projekt je prejel sredstva iz raziskovalnega in inovacijskega programa Evropske unije Obzorje 2020 v okviru pogodbe št. 745936.

Avtorji se zahvaljujemo za finančno podporo Javni agenciji za raziskovalno dejavnost Republike Slovenije (financiranje raziskovalnega programa št. P4-0015, "Les in lignocelulozni kompoziti").

Supplemental information and raw data:

Supplemental material and all raw data can be accessed openly via the author's institutional repository at https://repozitorij.uni-lj.si/IzpisGradiva.php?lang=slv&id=121368, and cited as Dahle et al. (2020).

Dodatne informacije in neobdelani podatki:

Dodatni material in vsi osnovni podatki, ki so na voljo v odprtem dostopu prek avtorjevega institucionalnega repozitorija na spletni strani https://repozitorij.uni-lj.si/IzpisGradiva.php?lang=slv&id=121368, naj bodo citirani Dahle et al. (2020).

REFERENCES
LITERATURA

Altgen, D., Bellmann, M., Wascher, R., Viöl, W., & Mai, C. (2015). Enhancing mechanical properties of particleboards using plasma treated wood particles. Eur. J. Wood Prod., 73: 219-223.

Altgen, D., Avramidis, G., Viöl, W., & Mai, C. (2016). The effect of air plasma treatment at atmospheric pressure on thermally modified wood surfaces. Wood Sci. Technol., 50:1227–1241.

Altgen, D., Grigsby, W., Altgen, M., Rautkari, L., & Mai, C. (2019). Analyzing the UF resin distribution in particleboards by confocal laser microscopy. Composites, Part A, 125:105529.

Bardak, S., Sarı, B., Nemli, G., Kırcı, H., & Baharoğlu, M. (2011). The effect of décor paper properties and adhesive type on some properties of particleboard. International Journal of Adhesion & Adhesives, 31:412-415.

Blanchard, V., Blanchet, P., & Riedl, B. (2009). Surface energy modification by radiofrequency inductive and capacitive plasmas at low pressures in sugar maple: An exploratory study. Wood and Fiber Science, 41(3):245-254.

Boero, F., Fedeli, A., Lamini, M., Maffongelli, M., Monleone, R., Pastorino, M., Randazzo, A., Salvadè, A., & Sansalone, A. (2018). Microwave tomography for the Inspection of wood materials: Imaging system and experimental results. IEEE Trans. Microw. Theory, 66(7):3497-3510.

Dahle, S., Žigon, J., Petrič, M., & Kariž, M. (2020). Plasma treatment of spruce wood changes its dielectric properties: research data underlying the article. (10. 11. 2020). Retrieved from https://repozitorij.uni-lj.si/IzpisGradiva.php?lang=slv&id=121368

Daian, G., Taube, A., Birnboim, A., Daian, M., & Shramkov, Y. (2006). Modeling the dielectric properties of wood. Wood Sci. Technol, 40:237-246. DOI: https://doi.org/10.1007/s00226-005-0060-7

Dam, T. N. (2017). Environmental enhancing adhesion properties of Wood-Plastic Composites by plasma at atmospheric pressure. 2017 International Conference on System Science and Engineering (ICSSE), 652-655. ISBN: 978-1-5386-3422-6. DOI: https://doi.org/10.1109/ICSSE.2017.8030956

De Cademartori, P. H. G., Carvalho, A. R., Marangoni, P. R. D., Berton, M. A. C., Blanchet, P., Muniz, G. I. B., & Magalhães, W. L. E. (2016). Adhesion performance and film formation of acrylic emulsion coating on medium density fiberboard treated with Ar plasma. International Journal of Adhesion & Adhesives, 70:322-328.

Gamaleev, V., Iwata, N., Hori, M., Hiramatsu, M., & Ito, M. (2019). Direct Treatment of Liquids using low-current arc in ambient air for biomedical applications. Appl. Sci., 9(17):3505. DOI: https://doi.org/10.3390/app9173505

Haase, J. G., Leung, L. H., & Evans, P. D. (2019). Plasma pre-treatments to improve the weather resistance of polyurethane coatings on black spruce wood. Coatings, 9(1):8.

Istek, A., Aydemir, D., & Aksu, S. (2010). The effect of décor paper and resin type on the physical, mechanical, and surface quality properties of particleboards coated with impregnated décor papers. BioResources, 5(2):1074-1083.

Jamali, A., & Evans, P. D. (2011). Etching of wood surfaces by glow discharge plasma. Wood Science and Technology, 45:169-182.

James, W. L. (1975). Dielectric properties of wood and hardboard: variation with temperature, frequency, moisture content, and grain orientation (Vol. 245). Department of Agriculture, Forest Service, Forest Products Laboratory.

Keskin, H., & Tekin, A. (2011). Abrasion resistances of cellulosic, synthetic, polyurethane, waterborne and acidhardening varnishes used woods. Constr. Build. Mater., 25:638-643.

Kranbuehl DE (1997). In: Dielectric spectroscopy of polymeric materials: fundamentals and applications, ACS, 1997. p. 303.

Král, P., Ráhel, J., Stupavská, M., Šrajer, J., Klímek, P., Mishra, K.P., & Wimmer, R. (2015). XPS depth profile of plasma–activated surface of beech wood (*Fagus sylvatica*) and its impact on polyvinyl acetate tensile shear bond strength. Wood Sci. Technol., 49:319-330.

Liston, E. M., Martinu, L., & Wertheimer, M. R. (1993). Plasma surface modification of polymers for improved adhesion: a critical review. J. Adhes. Sci. Technol., 7(10):1091-1127.

Nikolova, B. M., Nikolov, G. T., Gieva, E. E., & Ruskova, I. N. (2018). Dielectric Properties Measurement of Flexible Substrates. Proc. XXVII International Scientific Conference Electronics - ET2018, September 13 - 15, 2018, Sozopol, Bulgaria.

Norimoto, M., & Yamada, T. (1972). Dielectric Properties of Wood VI: On the Dielectric Properties of the chemical constituents of wood and the dielectric anisotropy of wood. Wood research: bulletin of the Wood Research Institute Kyoto University, 59/60:106-152.

Norimoto, M. (1976). Dielectric properties of wood. Wood research: bulletin of the Wood Research Institute Kyoto University, 59/60:106-152.

Nemli, G., & Hiziroglu, S. (2009). Effect of press parameters on scratch and abrasion resistance of overlaid particleboard panels. J. Compos. Mater., 43(13):1413-1420.

Perisse, F., Menecier, S., Duffour, E., Vacher, D., Monier, G., Destrebecq, J.-F., Czarniak, P., Górski, J., & Wilkowski, J. (2017). MDF treatment with a Dielectric Barrier Discharge (DBD) torch. Int. J. Adhes. Adhes., 79:18-22.

Rehn, P., & Viöl, W. (2003). Dielectric barrier discharge treatments at atmospheric pressure for wood surface modification. Holz Roh- Werkst., 61:145–150.

Reinprecht, L., Tiňo, R., & Šomšák, M. (2018). Adhesion of coatings to plasma modified wood at accelerated weathering. In: European Conference on Wood Modification 2018 (ECWM9), Arnhem, The Netherlands (On-line Proceedings). Ed. Creemers, J., Houben, T., Tjeerdsma, B., Militz, H., Junge, B., Gootjes, J., 205-209.

Rolleri, A., & Roffael, E. (2010). Influence of the surface roughness of particleboards and their performance towards coating. Maderas ciencia y tecnologia, 12(2):143-148.

Šernek, M., & Kamke, F. A. (2007). Application of dielectric analysis for monitoring the cure process of phenol formaldehyde adhesive. International Journal of adhesion and adhesives, 27(7), 562-567.

Sikder, S. S., Uddin, K. A., Rahman, M. M., & Bhuiyan, A. H. (2009). Effect of salinity on dynamic dielectric properties of Sundori wood of Bangladesh. Bangladesh J. Phys., 7-8:55-61.

Torgovnikov, G. I. (1993). Dielectric properties of wood-based materials. In Dielectric Properties of Wood and Wood-Based Materials, (pp. 135-159). Springer, Berlin, Heidelberg.

Veigel, S., Grüll, G., Pinkl, S., Obersriebnig, M., Müller, U., & Gindl-Altmutter, W. (2014). Improving the mechanical resistance of waterborne wood coatings by adding cellulose nanofibers. React. Funct. Polym., 85:214-220.

Wascher, R., Avramidis, G., Vetter, U., Damm, R., Peters, F., Militz, M., & Viöl, W. (2014). Plasma induced effects within the bulk material of wood veneers. Surface & Coatings Technology, 259:62-67.

Wolf, R., & Sparavigna, A. C. (2010). Role of plasma surface treatments on wetting and adhesion. Engineering, 2:397-402.

Wolkenhauer, A., Militz, H., & Viöl, W. (2008). Increased PVA-glue adhesion on particle board and fibre board by plasma treatment. Holz Roh- Werkst., 66:143-145.

Wolkenhauer, A., Avramidis, G., Hauswald, E., Loose, S., Viöl, W., & Militz, H. (2009). Investigations on the drying behaviour of adhesives on plasma-treated wood materials. Wood Res., 54(1):59-66.

Žigon, J., Petrič, M., & Dahle, S. (2018). Dielectric barrier discharge (DBD) plasma pretreatment of lignocellulosic materials in air at atmospheric pressure for their improved wettability: a literature review. Holzforschung, 72(11):972–911.

Žigon, J., Petrič, M., & Dahle, S. (2019a). Artificially aged spruce and beech wood surfaces reactivated using FE-DBD atmospheric plasma. Holzforschung, 73(12), 1069-1081.

Žigon, J., Zaplotnik, R., Ayata, Ü., Petrič, M., & Dahle, S. (2019b). The influence of artificial weathering and treatment with FE–DBD plasma in atmospheric conditions on wettability of wood surfaces. 3. Niedersächsisches Symposium Materialtechnik, Clausthal, 14. bis 15. Februar 2019. Tagungsband 3. Niedersächsisches Symposium Materialtechnik 7:559.