BEECH WOOD MODIFIED BY RADIO-FREQUENCY DISCHARGE PLASMA

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ABSTRACT

The radio-frequency discharge plasma (RFDP) has been used to improve the wetting and adhesive properties of beech (*Fagus Sylvatica* L.) wood. The pre-treatment of wood surface using discharge plasma is attractive for various wood applications, mainly because of its high efficiency and low production cost. Moreover, a significant increase of the polar component of wood surface energy after modification by RFDP has been identified, while the polar component of the surface energy is associated with the presence of acid-base forces (electron donor–acceptor bonds). The surface energy of beech wood pre-treated by RFDP during 120 s in air significantly decreased. The shear strength of adhesive joint beech wood-polyurethane adhesive increased non-linearly from 5.2 MPa (native beech wood) up to 7.8 MPa. FTIR-ATR results confirm the increase of the beech wood polarity during RFDP treatment due to growth in –OH polar groups amount. The enhancement of the wood wettability is a necessary condition to promote a better adhesion with a water-based adhesives and coatings, which is currently being studied.

Key words: adhesion, beech wood, plasma treatment, surface chemistry, hydrophilicity.

INTRODUCTION

The radio-frequency discharge plasma (RFDP) used for a treatment of the wood surface lead to an increase of the adhesion of wood to various substrates by adhesives (Wolkenhauer *et al.* 2009, Acda *et al.* 2012). There are two reasons why discharge plasma can be applied and leads to the surface treatment. Firstly, discharge plasma in air significantly increases hydrophilicity of the wood because of formation various polar groups (e.g. hydroxyl, carbonyl, carboxyl groups, etc.), and the wood macromolecules are also cross-links (up to a few microns), what leads to the increase in scratch resistance, and to the improvement in barrier properties of the wood material (Rehn *et al.* 2003, Moghadamzadeh *et al.* 2011). Second reason for the plasma use is an increase of adhesion in adhesive joint between polymeric adhesive and wood substrate due to growth of wood wettability, that is important for industrial applications. The RFDP working at reduced press 100 Pa in air as processing gas is considered as a "green" and ecological friendly method (Odrášková *et al.* 2008, Müller *et al.* 2009). For a common industrial wood application various woods have to possess a large set of various surface characteristics, including polarity (hydrophobicity or hydrophilicity), dyeability, scratch resistance, tailored adhesive properties, antibacterial resistance etc.

This contribution is focused on a study of the surface, and adhesive properties as well as on analysis of chemical changes of plasma modified beech wood, namely polar groups, of the beech wood modified by the RFDP.

EXPERIMENTAL METHODS

MATERIALS

Beech wood (*Fagus Sylvatica* L.) plates with dimensions 50 × 15 × 5 mm (Technical University in Zvolen, Slovakia) with 8% of humidity, water-based polyurethane adhesive Dispercoll U 53 (Bayer, Germany), twice distilled water was used as a testing liquid, and dichloro methane (Fluka, Germany) for degreasing of the surface.

PLASMA MODIFICATION METHOD

The surface of beech wood sample was modified by RFDP in air (Slovak Academy of Sciences). The modification of wood by the capacitive coupled RFDP was performed in a laboratory plasma system working at reduced pressure 100 Pa consists of two 240 mm brass parallel circular electrodes with symmetrical arrangement, and 10 mm thick, between which RFDP was created. The electrodes of RFDP system are placed in a locked-up stainless steel vacuum cylinder. The voltage of RFDP reactor is 2 kV, frequency 13.56 MHz, max. current intensity is 0.6 mA, and the max. power of the plasma source is 1200 W. The wood samples were modified by RFDP at the power 300 W.

MEASUREMENTS METHODS

The hydrophilicity of beech wood was measured by contact angles determination using twice distilled water, the drop volume was 20 µm. Contact angle of the beech wood was determined by professional Surface Energy Evaluation (SEE) contact angle meter equipped with a web camera (Advex, Czech Republic), and necessary PC software.

The shear strength of plasma-treated beech wood to polyurethane adhesive was tested with overlapped adhesive joints in universal testing machine Instron 4301 (Instron, England) equipped with 5 kN force chamber.

Fourier Transform Infrared Spectroscopy Attenuated Total Reflectance (FTIR-ATR) measurements were performed with an FTIR Nicolet TM spectrometer (Thermo Scientific, USA) using a single bounce ATR accessory equipped with a Ge crystal. For each measurement, the spectral resolution was 2 $cm^{-1}$and 64 scans were performed.

RESULTS AND DISCUSSION

The contact angle of water drop on the beech wood surface was measured 3 s after drop deposition due to thermo-dynamical equilibrium achievement. The contact angle of water on beech wood surface modified by RFDP in air vs. activation time is shown in Fig. 1.

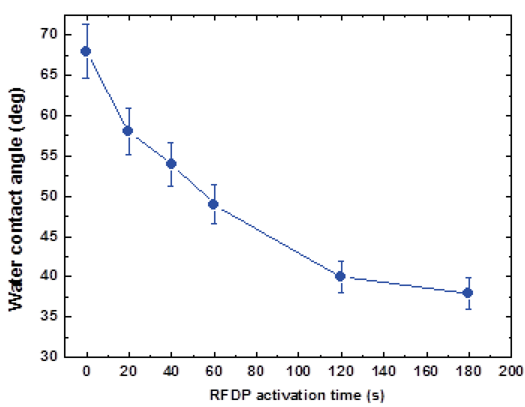

Figure 1: Water contact angle on beech wood surface modified by RFDP in air vs. activation time

The contact angles of water decreased with time of the activation by RFDP in air (Fig. 1), and showed a steep decrease from 66° (native beech wood) to 40° after 120 s activation of beech wood by RFDP. The decrease of the contact angle of polar testing liquid (water) can be explained by an increase of the hydrophilicity of beech wood surface during pre-treatment by RFDP. The hydrophilicity of the wood surface depends on the formation of polar oxygenic functional groups during plasma modification of wood in air. After saturation of the wood surface with polar groups the hydrophilicity was stabilized.

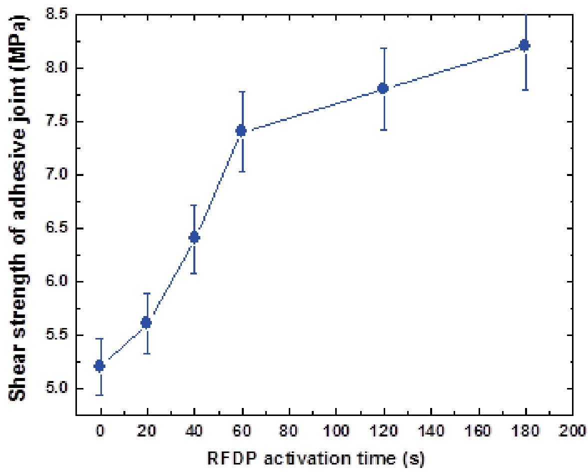

Figure 2: Shear strength of the adhesive joint beech wood-polyurethane after treatment of wood by RFDP in air vs. activation time

The shear strength of adhesive joint beech wood modified by RFDP in air – polyurethane adhesive vs. activation time is shown in Figure 2. The shear strength of adhesive joint beech wood-polyurethane increases non-linearly from 5.2 MPa (native beech wood) to 7.8 MPa (120 s activation by RFDP). The increase of the strength of adhesive joint beech wood-polyurethane-beech wood is depending on surface energy of the wood as well as on the topography/roughness of the wood surface.

Table 1 contains the results of normalized FTIR of beech wood modified by RFDP in air for different treatment time. The calculations with modified FTIR spectra were multiplied by a specific factor in order to have better readability common range of FTIR spectra. After this modification one can more clearly see the subtle changes in FTIR spectra the subtle changes in the shape of lines of C=O and C–O–C bonds, which confirm the changes that occurred on the wood surface. To quantify these changes following procedure have been realized: the integrated intensity ratios of polar –OH groups with a maximum at 3400 cm^{-1} and of non-polar CH_2 groups with a maximum at 2985 cm^{-1} $(–CH_2)_{sym}$ were estimated. Table 1 shows the ratios of the integrated intensities with $P(OH)/P(–CH_2)$, where the vibration of $–CH_2–$ was chosen as an internal standard with that assumption, that the plasma treatment does not affect this area. An increase of the ratio $P(OH)/P(–CH_2)$ during plasma treatment of the beech wood was observed. The ratio $P(OH)/P(–CH_2)$ correlates with time of plasma treatment. The significant increase of the integrated intensities ratio was observed from value 10.5 (native wood) up to value 28.3 (RFDP-treated wood, 120 s).

Table 1: Ratio of integrated intensities P(OH)/P(CH_2) of beech wood modified by RFDP in air calculated from FTIR-ATR spectra

Beech wood	P(2895, CH_2 stretch)	P(3400, OH stretch)	P(OH)/P(CH_2)
Native	0.496	5.203	10.490
RFDP, 40 s	0.286	5.811	20.318
RFDP, 80 s	0.264	6.512	24.667
RFDP, 120 s	0.244	6.913	28.332

CONCLUSIONS

The surface energy of beech wood treated by RFDP in air during 120 s decreased from 66 to 40°. The shear strength of adhesive joint beech wood-polyurethane increases non-linearly from 5.2 MPa (native beech wood) to 7.8 MPa (120 s activation by plasma). FTIR-ATR results confirm the increase of the beech wood polarity during RFDP treatment due to growth in –OH groups amount.

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MODIFICATION OF VARIOUS WOOD SPECIES BY BARRIER DISCHARGE PLASMA

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ABSTRACT

The barrier discharge plasma (BDP) modification represents an appropriate method for the polarity increasing of the wood surfaces. The surface properties of various wood species (beech, maple, birch) were pre-treated using BDP at atmospheric pressure in air were evaluated by contact angle measurements. The FTIR spectrum of the three tested species of wood is a mixed spectrum (composition) of cellulose and lignin with characteristic peaks corresponding to –OH bonds (with a maximum at about 3400 cm^{-1}) and fingerprints assigned to the –CO, –COO and $–CH_2–$ bonds typical for polysaccharides.

Key words: barrier discharge plasma, beech, maple, birch, chemical composition.

INTRODUCTION

The using of the low-temperature plasma for wood modification leads to an improvement of the wood adhesion to various substrates by adhesives (Hünnekens *et al.* 2018). The discharge plasma in air significantly increases hydrophilicity of the wood because of formation various polar groups (e.g. hydroxyl, carbonyl, carboxyl, etc.), and the wood macromolecules are also cross-links (up to a few microns), what leads to the increase in scratch resistance, and to the improvement in barrier properties of the wood. After discharge plasma modification of the wood we can observe an increase of adhesion in adhesive joint between wood substrate and adhesive due to growth of wood hydrophilicity, important for industrial applications. The low-temperature plasma represents a mixture of various excited particles, such as ions, atoms, electrons, and radicals, and plasma created particles have sufficient levels of energy to break chemical bonds in the wood substrate (Novák *et al.* 2016). The treatment of the wood by discharge plasma is limited to a few nanometres without affecting the bulk properties of the wood (Acda *et al.* 20012). The increased surface polarity due to oxidations reaction during modification of wood by RF plasma improves its wettability and hydrophilicity (Ciolacu *et al.* 2011). The wettability helps in establishing a molecular scale contact with the wood surface and critical to the development of strong adhesion at the adhesive/wood interface. Great efforts have been made in developing various kinds of furniture using wood or plastics veneers in adhesive joints wood-adhesive-veneer (Kúdela *et al.* 2017). The barrier discharge plasma (BDP) at atmospheric pressure is currently an efficient method for modification of surface and adhesive properties of the wood, and is considered as a “green” and ecological friendly modification method (Moghadamzadeh *et al.* 2011). This paper is focused on a study of the surface properties of selected wood species as well as on changes in chemical composition of the plasma modified wood.

EXPERIMENTAL METHODS

MATERIALS

Beech (*Fagus Sylvatica* L.), birch (*Betula Pendula* L.), and maple (*Acer Pseudoplatanus*) wood plates with dimensions 50 × 15 × 5 mm (Technical University in Zvolen, Slovakia) with 8% of humidity, twice distilled water as a testing liquid for contact angles measurement.

BARRIER DISCHARGE PLASMA TREATMENT

The surface of selected wood species was pre-treated by barrier discharge plasma (Fig. 1). The BDP set-up was operated at 350 W under atmospheric pressure in air. Two parallel banded systems of electrodes made of Ag paste (1 mm wide and 50 μm thick, with 0.5 mm spacing between the strips) generated the low-temperature plasma in an effective manner. The electrodes were embedded in 96% Al_2O_3, which protected the electrodes from direct contact with the plasma and thereby prolonged their lifetime. The plasma panel was also connected to a cooling system to prevent overheating. A high-frequency sinusoidal voltage (~15 kHz, with a U_m of ~10 kV) applied to the electrodes led to macroscopically homogenous plasma generation and uniform surface treatment.

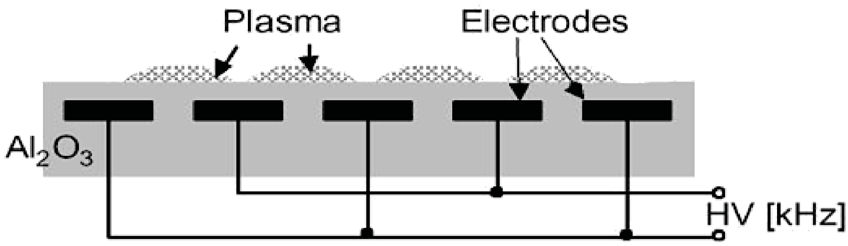

Figure 1: Barrier discharge plasma set-up

FTIR-ATR

Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance (FTIR-ATR) measurements were performed with an FTIR Nicolet 8700 spectrometer (Thermo Scientific, UK) using a single bounce ATR accessory equipped with a Ge crystal. For each measurement, the spectral resolution was 2 $cm^{-1}$and 64 scans were performed.

RESULTS AND DISCUSSION

The results of water contact angles on the surface of the investigated three wood species versus time of modification by BDP is shown in Fig. 2. The contact angles of water in the investigated wood surfaces diminished with the time of modification by BDP, and showed a steep decrease from 72° (beech wood) to 50° after modification by plasma for 120 s. The hydrophilicity (polarity) of the wood surface depends on the polar oxygenic functional groups formation during plasma treatment of wood in air. After saturation (from 60 s of the plasma treatment) of the wood surface with polar groups, the wood hydrophilicity was stabilized. The deeper decrease (from 70° up to 30°) of contact angles was observed for birch and maple wood modified by BDP.

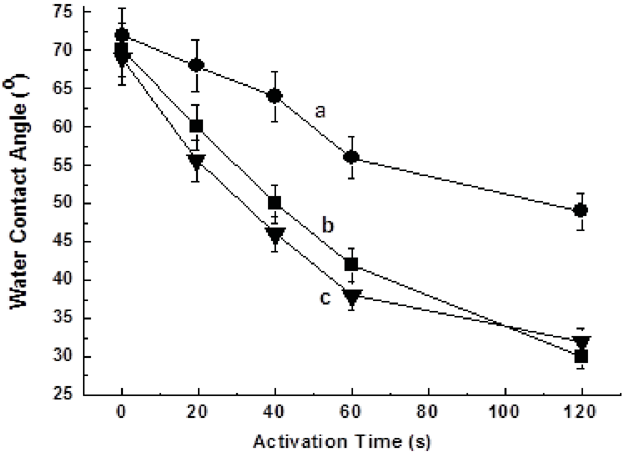

Figure 2: Water contact angle of selected wood species wood surface treated by BDP in air vs. plasma activation time: a – beech wood, b – birch wood, c – maple wood

The FTIR spectrum of selected wood species represents a mixed spectrum of cellulose and lignin with characteristic peaks in –OH bonds with a maximum at about 3400 cm^{-1}, so as in the area of fingerprints, which is reflected oxygen bonds in groups in C–O–C, COO, and unpolar CH_2 bonds typical for polysaccharides. The peak (C–O–C) appears for each of them as typical representative. Ratios of integrated intensities of oxygen bonding groups (with the majority contribution of –OH groups) with their maximum at 3400 cm^{-1} and integrated intensities at the 2985 cm^{-1} (CH_2)sym were determined. However, this is only semi quantitative information, Table 1 shows ratios of integrated intensities P(–OH)/P(–CH_2), where the vibration of –CH_2– was chosen as an internal standard with the assumption that the plasma treatment does not affect this area.

Table 1: The ratio of integrated peaks for P (2895, CH_2 stretch) and P (3400, OH stretch) calculated from FTIR for selected wood species treated by BDP

BDP treatment time (s)	P(OH)/P(CH_2) Beech	P(OH)/P(CH_2) Birch	P(OH)/P(CH_2) Maple
unmodified	8.474	6.627	5.948
20 s	13.973	10.135	11.914
40 s	20.624	14.690	14.046
60 s	22.986	18.632	16.960

In Table 1 we can observed an increase of P(OH)/P(CH_2) ratio with plasma treatment time, that shows also an increase of the polarity of selected wood species. The largest increase was observed in the case of beech wood (from value of 8.474 for the untreated beech wood up to 22.986 for the 60 s plasma treatment. The ratio P(OH)/P(CH_2) for untreated types of woods ranges from 5.948 to 8.474, which indicates approximately the same hydrophilicity, that is, the content of –OH groups on the surface of all types of wood before any treatment was the same. It can be concluded that FTIR-ATR measurements confirmed that the plasma treatment causes some changes at the surface of all types of wood, which are dependent on the time of exposition by plasma and it can be said that there is an increased content of hydrophilic groups compared to the untreated samples. Conclusions from the FTIR-ATR spectroscopy could be complemented by measuring of contact angles of plasma treated wood species as well.

CONCLUSIONS

The contact angle of water of selected wood species modified by BDP in air decreased significantly with plasma treatment time, Results of ATR-FTIR spectra measurement confirms the increase of the wood polarity and hydrophylicity after BDP treatment due to growth in –OH group amount. The content of oxygenic polar groups on the surface of wood after plasma treatment increased, but the amount of carbon conversely decreased. The concentration of –C–O, COOH, and C=O polar groups after treatment by BDP significantly increased.

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