

## MODIFICATION OF VARIOUS WOOD SPECIES BY BARRIER DISCHARGE PLASMA

Ján Sedliačik<sup>1</sup>, Igor Novák<sup>2</sup>, Ivan Chodák<sup>2</sup>, Angela Kleinová<sup>2</sup>, Ján Matyašovský<sup>3</sup>,  
Peter Jurkovič<sup>3</sup>

<sup>1</sup>Technical University in Zvolen, Zvolen, Slovakia,

<sup>2</sup>Slovak Academy of Sciences, Bratislava, Slovakia,

<sup>3</sup>VIPO a.s., Partizánske, Slovakia

e-mail: sedliacik@tuzvo.sk; igor.novak@savba.sk; jmatyasovsky@vipo.sk

### 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<sup>-1</sup>) and fingerprints assigned to the –CO, –COO and –CH<sub>2</sub>– 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 Pseudo-platanus*) wood plates with dimensions  $50 \times 15 \times 5$  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  $50 \mu\text{m}$  thick, with 0.5 mm spacing between the strips) generated the low-temperature plasma in an effective manner. The electrodes were embedded in 96%  $\text{Al}_2\text{O}_3$ , 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 ( $\sim 15$  kHz, with a  $U_m$  of  $\sim 10$  kV) applied to the electrodes led to macroscopically homogenous plasma generation and uniform surface treatment.

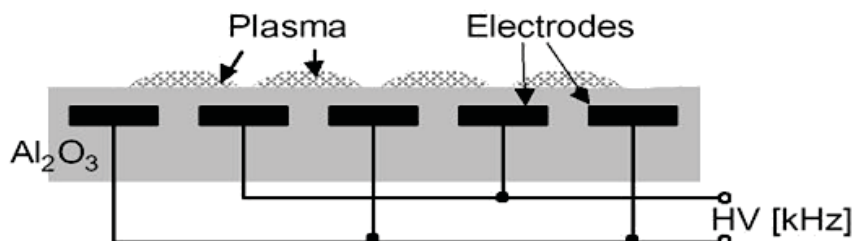


Figure 1: Barrier discharge plasma set-up

### 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  $2 \text{ cm}^{-1}$  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  $72^\circ$  (beech wood) to  $50^\circ$  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  $70^\circ$  up to  $30^\circ$ ) of contact angles was observed for birch and maple wood modified by BDP.

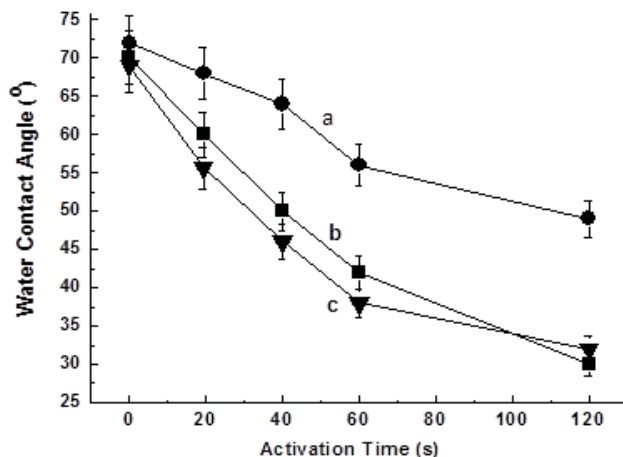


Figure 2: Water contact angle of selected wood species wood surface treated by BDP in air vs. plasma activation time: a – beech wood, b – birch wood, c – maple wood

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  $3400\text{ cm}^{-1}$ , so as in the area of fingerprints, which is reflected oxygen bonds in groups in C–O–C, COO, and unpolar  $\text{CH}_2$  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  $3400\text{ cm}^{-1}$  and integrated intensities at the  $2985\text{ cm}^{-1}$  ( $\text{CH}_2$ )<sub>sym</sub> were determined. However, this is only semi quantitative information, Table 1 shows ratios of integrated intensities  $\text{P}(\text{OH})/\text{P}(\text{CH}_2)$ , where the vibration of – $\text{CH}_2$ – 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,  $\text{CH}_2$  stretch) and P (3400, OH stretch) calculated from FTIR for selected wood species treated by BDP

BDP treatment time (s)	$\text{P}(\text{OH})/\text{P}(\text{CH}_2)$		$\text{P}(\text{OH})/\text{P}(\text{CH}_2)$
	Beech	Birch	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  $\text{P}(\text{OH})/\text{P}(\text{CH}_2)$  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  $\text{P}(\text{OH})/\text{P}(\text{CH}_2)$  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.

### ACKNOWLEDGEMENTS

This work was supported by the Slovak Research and Development Agency under the contracts No. APVV-16-0177, APVV-20-0159, APVV-21-0051, VEGA 1/0264/22 and VEGA 2/0019/19.

### REFERENCES

- ACDA M.N., DEVERA E.E., CABANGON R.J., RAMOS H.J. 2012. Effects of plasma modification on adhesion properties of wood. *International Journal of Adhesion and Adhesives*, 32: 70–75.
- CIOLACU D., CIOLACU F., POPA V.I. Amorphous cellulose: Structure and characterization. *Cellulose Chemistry and Technology*, 45: 13–21.
- HÜNNKENS B., AVRAMIDIS G., OHMS G., KRAUSE A., VIÖL W., MILITZ H. 2018. Impact of plasma treatment under atmospheric pressure on surface chemistry and surface morphology of extruded and injection-molded wood-polymer composites (WPC). *Applied Surface Science*, 441: 564–574.
- KÚDELA J., ŠTRBOVÁ M., JAŠ F. 2017. Influence of accelerated ageing on morphology and wetting of wood surface treated with a modified water-based coating system. *Acta Facultatis Xylogologiae Zvolen*, 59, 1: 27–39.
- MOGHADAMZADEH H., RAHIMI H., ASADOLLAHZADEH M., HEMMATI A.R. 2011. Surface treatment of wood polymer composites for adhesive bonding. *International Journal of Adhesion and Adhesives*, 31: 816–821.
- NOVÁK I., SEDLIAČIK J., GAJTANSKA M., SCHMIDTOVÁ J., POPELKA A., BEKHTA P., KRYSŤOFIAK T., PROSZYK S., ŽIGO O. 2016. Effect of barrier plasma pre-Treatment on polyester films and their adhesive properties on oak wood. *BioResources*, 11, 3: 6335–6345.



UNIVERSITY OF FORESTRY

-----  
FACULTY OF FOREST INDUSTRY



# **INNOVATION IN WOODWORKING INDUSTRY AND ENGINEERING DESIGN**

## **1/2023**

INNO vol. XII Sofia

ISSN 1314-6149  
e-ISSN 2367-6663

Indexed with and included in CABI

# INNOVATION IN WOODWORKING INDUSTRY AND ENGINEERING DESIGN

Science Journal  
Vol. 12/ p. 1–80  
Sofia 1/2023

ISSN 1314-6149  
e-ISSN 2367-6663

Edition of  
**FACULTY OF FOREST INDUSTRY – UNIVERSITY OF FORESTRY – SOFIA**

**The Scientific Journal is indexed with and included in CABI.**

## SCIENTIFIC EDITORIAL BOARD

Alfred Teischinger, PhD (Austria)	Marius Barbu, PhD (Romania)
Alexander Petutschning, PhD (Austria)	Muhammad Adly Rahandi Lubis, PhD (Indonesia)
Anna Danihelová, PhD (Slovakia)	Nencho Deliiski, DSc (Bulgaria)
Antonios Papadopoulos, PhD (Greece)	Neno Tritchov, PhD (Bulgaria)
Asia Marinova, PhD (Bulgaria)	Pavlin Vitchev, PhD (Bulgaria)
Biborka Bartha, PhD (Romania)	Pavlo Bekhta, PhD (Ukraine)
Bojidar Dinkov, PhD (Bulgaria)	Petar Antov, PhD (Bulgaria)
Danijela Domljan, PhD (Croatia)	Regina Raycheva, PhD (Bulgaria)
Desislava Angelova, PhD (Bulgaria)	Roman Réh, PhD (Slovakia)
Derya Ustaömer, PhD (Turkey)	Ružica Beljo Lučić, PhD (Croatia)
George Mantanis, PhD (Greece)	Silvana Prekrat, PhD (Croatia)
Ivica Grbac, PhD (Croatia)	Štefan Barčík, PhD (Slovakia)
Ivo Valchev, PhD (Bulgaria)	Svetoslav Anev, PhD (Bulgaria)
Ján Sedliačik, PhD (Slovakia)	Valentin Shalaev, PhD (Russia)
Julia Mihajlova, PhD (Bulgaria)	Vasiliki Kamperidou (Greece)
Hubert Paluš, PhD (Slovakia)	Vesselin Brezin, PhD (Bulgaria)
Hülya Kalaycioğlu, PhD (Turkey)	Victor Savov, PhD (Bulgaria)
Ladislav Dzurenda, PhD (Slovakia)	Vladimir Koljozov, PhD (Macedonia)
Luboš Krišták, PhD (Slovakia)	Zhivko Gochev, PhD (Bulgaria)

## EDITORIAL BOARD

N. Trichkov, PhD – Editor in Chief	V. Savov, PhD
D. Angelova, PhD – Co-editor	P. Vitchev, PhD
N. Minkovski, PhD	

Cover Design: **DESI SLAVA ANGELOVA**

Printed by: **INTEL ENTRANCE**

Publisher address: **UNIVERSITY OF FORESTRY – FACULTY OF FOREST INDUSTRY**  
**Kliment Ohridski Bul., 10, Sofia, 1797, BULGARIA**  
<http://inno.ltu.bg>  
<http://www.scjournal-inno.com/>

## CONTENTS

DESIGNING AN ICONOSTASIS OF AN ORTHODOX CHURCH.....	5
Asparuh Atanasov, Aleksandrina Bankova	
DATA ENVELOPMENT ANALYSIS OF FACTORS FOR FOREST INDUSTRY WAGES AND SALARIES LEVELS IN NUTS 2 REGIONS OF BULGARIA.....	12
Nikolay Neykov, Radostina Popova-Terziyska, Emil Kitchoukov	
INVESTIGATION OF THE INFLUENCE OF SOME FACTORS ON THE STRENGTH AND STIFFNESS OF JOINTS WITH STAPLES AND GUSSET PLATES.....	18
Desislava Hristodorova, Nelly Staneva	
DEPENDENCE ON SHRINKAGE AND SWELLING IN CHEMICAL COMPOSITION AND ANATOMICAL STRUCTURE – AN OVERVIEW .....	25
Martina Todorova, Nikolai Bardarov	
REDUCTION OF FORMALDEHYDE EMISSION FROM WOOD-BASED PANELS BY MODIFICATION OF UF ADHESIVES WITH NATURAL BIOPOLYMERS.....	31
Ján Matyašovský, Ján Sedliačik, Peter Jurkovič, Peter Duchovič, Igor Novák	
MODERN ENGINEERING TECHNIQUES FOR THE PRODUCTION OF MODIFIED POLYSACCHARIDES WITH BIOLOGICAL ACTIVITY.....	41
Dragomir Vassilev, Nadezhda Petkova, Milka Atanasova, Panteley Denev	
SUNFLOWER STALKS AND LIGNOSULFONATE – ALTERNATIVE RAW MATERIALS FOR THE PRODUCTION OF ECO-FRIENDLY MEDIUM DENSITY FIBREBOARDS .....	47
Julia Mihajlova, Viktor Savov	
BEECH WOOD MODIFIED BY RADIO-FREQUENCY DISCHARGE PLASMA.....	58
Peter Jurkovič, Ján Sedliačik, Igor Novák, Ivan Chodák, Angela Kleinová, Ján Matyašovský	
MODIFICATION OF VARIOUS WOOD SPECIES BY BARRIER DISCHARGE PLASMA .....	62
Ján Sedliačik, Igor Novák, Ivan Chodák, Angela Kleinová, Ján Matyašovský, Peter Jurkovič	
APPLICATION OF ONLINE PLATFORMS IN TRAINING FOR THE DEVELOPMENT OF PROFESSIONAL DIGITAL COMPETENCES.....	66
Adelina Ivanova, Melina Neykova	
SCIENTIFIC JOURNAL „INNOVATIONS IN WOODWORKING INDUSTRY AND ENGINEERING DESIGN“ .....	78