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Modification of wood by radio-frequency discharge plasma

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Abstract: *Modification of wood by radio-frequency discharge plasma***.** Low-temperature plasma was used to improve the surface and adhesive properties of wood. The pre-treatment of wood surfaces using radio-frequency (RF) discharge plasma is attractive for various wood applications, mainly because of the high efficiency and low production cost of the process. The treatment of wood by RF plasma exhibited an aging effect, with the modified surface never recovering its initial hydrophobic state. The contact angle of water decreased with the activation time of the RF plasma treatment.

Keywords: radio-frequency discharge plasma, beech wood, adhesive properties

INTRODUCTION

The low-temperature plasma used to treat wood surfaces leads to improvements in the bonding of wood to various substrates via adhesives. There are two reasons why discharge plasma is applied for the surface treatment of wood. The discharge plasma in air alone significantly increases the hydrophilicity of wood due to the formation of various polar groups, and the macromolecules in wood serve as cross-links (measuring up to a few microns long), which leads to an increase in scratch resistance and to an improvement in the barrier properties of the wood material. The application of discharge plasma enhances the bonding of joints between polymeric adhesives and wood substrates due to the increase in the wettability of wood, which is important for industrial applications. A low-temperature plasma is a mixture of various excited particles, such as ions, atoms, electrons, and radicals, with low degrees of ionization and low penetrating energy; however, the particles in such as plasma have sufficient energy to break chemical bonds in wood substrates (Odrášková at al. 2008). The effects of the discharge plasma treatment of wood are limited to a few nanometers beneath the substrate surface and thus do not affect the bulk properties of wood (Novák at al. 2012). The increase in surface polarity due to oxidation reactions induced during the modification of wood by RF plasma improves the wettability and hydrophilicity of wood (Muller at al. 2009).

This contribution focuses on the more detailed investigation of the surface and adhesive properties, chemical composition, and physical changes of beech wood modified by RF discharge plasma. The chemical changes of RF plasma-treated beech wood were also investigated.

EXPERIMENTAL

Beech wood plates with 8% moisture content were modified by plasma (TU Zvolen, Slovakia). The surface of the beech wood samples was treated in air as processing gas by capacitively coupled RF discharge plasma source (Scheme 1) operated at a reduced pressure of 80 Pa. The system consists of two circular brass electrodes measuring 240 mm in diameter and 10 mm in thickness placed parallel to one another, between which RF plasma was created.

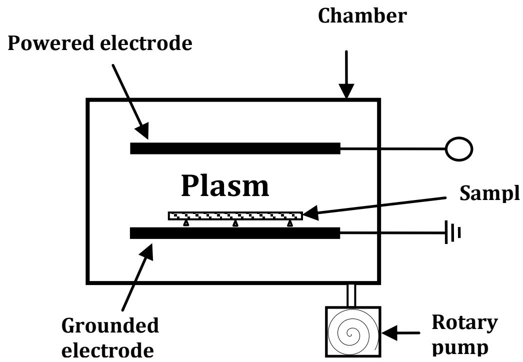


Figure 1. Scheme of RF discharge plasma source

The electrodes of the RF plasma system were placed in a sealed stainless steel vacuum cylinder, with one of the electrodes powered and the other one grounded to the steel cylinder. The voltage of the RF plasma reactor is 2 kV, the frequency 13.56 MHz, the maximum current intensity 0.6 mA, and the maximum power of the CCRF plasma source 1200 W. The wood samples were modified by RF plasma at the source power of 300 W.

The water contact angles of beech wood were measured using a professional SEE (Surface Energy Evaluation) device equipped with a web camera (Advex, Czech Republic) and the appropriate PC software of beech wood was determined by measuring the contact angles of a set of 5 test liquids. The water drops (V = 20 µl) were placed on the surface of the wood samples with a micropipette (Biohit, Finland) and value of contact angles were evaluated.

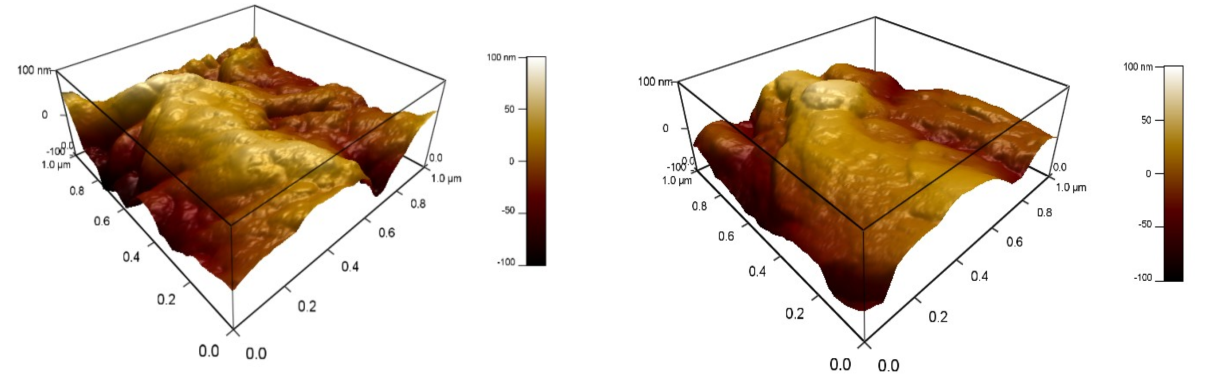
The surface morphology of the plasma-treated beech wood samples was measured by AFM. All measurements were performed under ambient conditions using a commercial atomic force microscope (NanoScope Dimension IIIa, MultiMode Digital Instruments, USA) equipped with a PPP-NCLR tapping-mode probe (Nanosensors, Switzerland; spring constant: 39 $N.m^{-1}$, resonant frequency ~ 180 kHz).

Nanoindentation analysis was performed using a Hysitron TriboLab Nanomechanical Test Instrument (Hisitron, USA) equipped with a scanning probe microscope and a Berkovich probe. The TI 750 Ubi nanomechanical test instrument is a dedicated scanning nanoindenter. The system is equipped with Hysitron's in situ SPM imaging capability and a performance control unit. The nanometer-resolution in situ imaging, tip-positioning ability, increased sensitivity, and feedback rate of the TI 750 Ubi and performance control unit allows for low displacement and high-resolution testing.

X-ray photoelectron spectroscopy (XPS) data were recorded using a Thermo Scientific K-Alpha XPS system (Thermo Fisher Scientific, UK) equipped with a micro-focused, monochromatic Al Kα X-ray source (1486.6 eV). An X-ray beam with a spot size of 400 µm size was used at 6 mA x 12 kV.

RESULTS AND DISCUSSION

Using AFM analysis, it was possible to observe the detailed 3D structure of the analysed surface. The surface roughness of the beech wood (Figure 2) represents a key factor that contributes to the mechanical interlocking phenomenon and substantially affects the strength of adhesive joint. After plasma treatment, the cellulose crystalline regions in beech wood will remain intact while amorphous lignin regions are ablated, thus leading to a smoother wood surface. Previous screening of the surface regularity was carefully carried out for the subsequently individual AFM measurements and obtaining representative results. The difference in the surface roughness between the untreated beech wood (Figure 2 A) and plasma-treated beech wood (Figure 2 B) was not clearly visible, but the roughness of the latter was lower (R_a = 18.7 nm) than that of the former (R_a = 21.8 nm). This conclusion is in good agreement with the ablation effects caused by the surface modification of wood surfaces via discharge plasma.

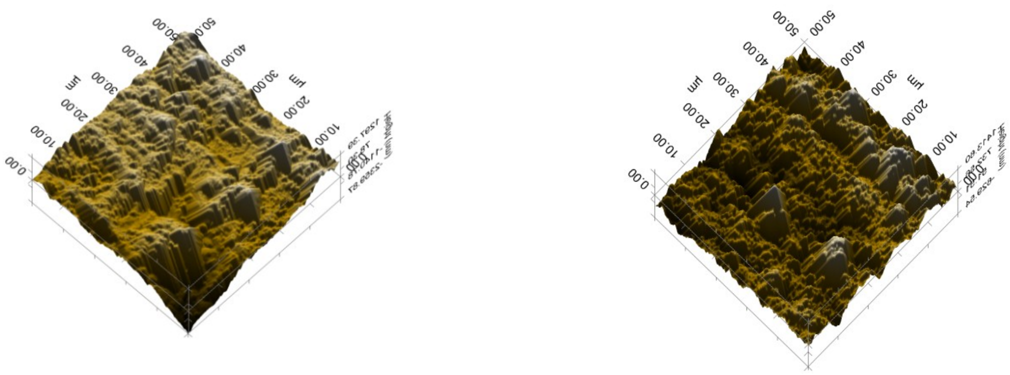


A **B**

Figure 2. 3D AFM images of beech wood: A – pristine sample (R_a = 21.8 nm), B – RF plasma-treated sample (R_a = 18.7 nm), 120 s (1000×1000 nm).

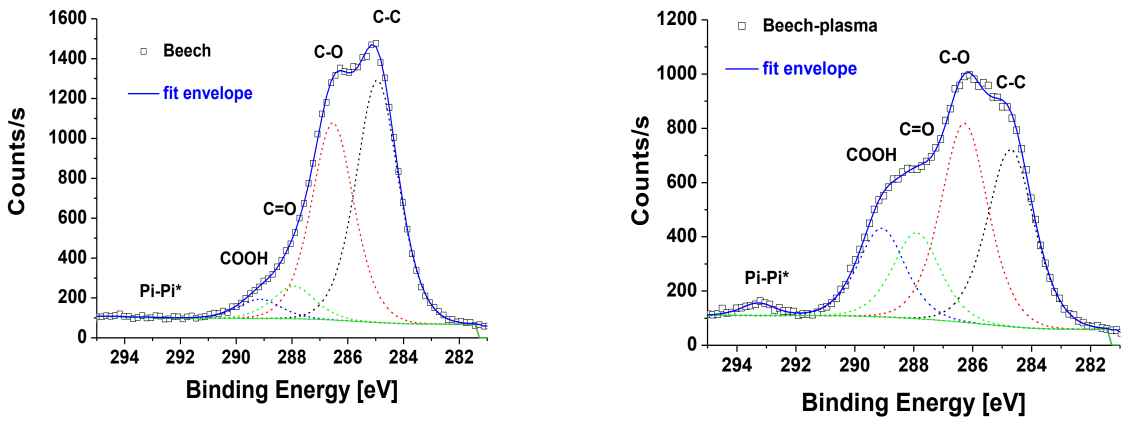
Nanoindentation analysis allowed for the investigation of the surface topography and roughness of the wood samples. The nanoindentation results are illustrated in Figure 2. The pristine beech wood sample, whose results are presented in Figure 3 A, exhibited similar roughness to that of beech wood treated by RF discharge plasma (Figure 3 B). The ablation processes induced during the modification of wood by RF plasma did not significantly alter the roughness of the beech wood surface. Based on the results illustrated in Figure 2, the changes in roughness values are not significant.

Figure 4 represent the XPS spectra of beech wood modified by RF plasma. Figure 4 A and Figure 4 B compare the carbon C1s peaks of untreated beech wood (A) and a RF plasma-treated (120 s) sample (B) obtained from XPS measurements. The spectrum of the untreated beech wood (Figure 3 A) shows two basic peaks, one attributed to C–C bonds at ~ 284.9 eV and the other associated with C–O bonds at ~ 286.5 eV; additionally, some minor peaks assigned to C=O at ~ 288.1 eV and COOH at ~ 289.1 eV bonds can be observed. After RF plasma treatment (Figure 3 B), there was an increase in the intensity of peaks corresponding to carbon-oxygen groups, especially those assigned to C=O and COOH groups.



A **B**

Figure 3. Nanoindentation analysis of beech wood: A – pristine sample, B – CCRF plasma modified sample, 120 s (50×50 nm).



A B

Figure 4. XPS spectra of beech wood modified by RF plasma (120 s): A – carbon C1s peak of pristine beech wood, B – carbon C1s peak of plasma-treated beech wood.

The XPS results obtained for beech wood treated by RF plasma (120s) are summarized in Table 1. The concentration of nitrogen in the air plasma was four times higher than that of oxygen, but the increase in the former after the modification of wood by RF plasma was lower than that in the latter. One reason for this result is the two-fold higher dissociation energy of nitrogen molecules relative to the dissociation energy of oxygen molecules, and thus the lower representation of dissociated molecules of nitrogen in the air plasma.

Table 1. Apparent surface chemical composition of beech wood modified by RF discharge plasma for 120 s as determined by XPS.

Beech wood	**Surface chemical composition [At.%]**			
	O1s	C1s *C1 s fit* *C-C, C-O, C=O, COOH, π→π**	N1s	Ca2p
pristine	26.1±0.6	72.8±0.5 52.9±3.5, 37.6.0±2.4, 6.2±0.4, 2.9±1.0, 0.3±0.1	0.9±0.2	0.3±0.1
plasma-treated	38.2±2.4	58.1±2.9 37.0±4.8, 34.4±1.7, 14.1±1.1, 13.4±2.2, 1.1±0.5	2.5±0.3	1.2±0.3

Another reason is the greater stability of the C–O bond compared with that of the C–N bond and thus the greater stability of the C=O bond versus the C=N bond. The concentration of oxygen on the beech wood surface after 120 s of RF plasma treatment increased s from 26.1 to 38.2 at. %, and the amount of nitrogen increased from 0.9 to only 2.5 at. %. The amount of carbon during the plasma treatment of the beech wood conversely decreased from 72.8 to 58.1 at. %.

The contact angle of water decreased with the activation time of the RF plasma treated beech wood (Figure 4) and showed a steep decrease from 66^{o} deg (pristine beech wood) to 40^{o} after 120 s of activation by RF plasma in air. The decrease in the contact angle of the polar test liquid (i.e. water) can be explained by the increase in the hydrophilicity of the beech wood surface during pre-treatment by RF plasma in air. The hydrophilicity of the wood surface depended on the formation of polar oxygenic functional groups during the plasma modification of the wood in air. After the saturation of the surface with polar groups, the hydrophilicity of the wood was stabilized.

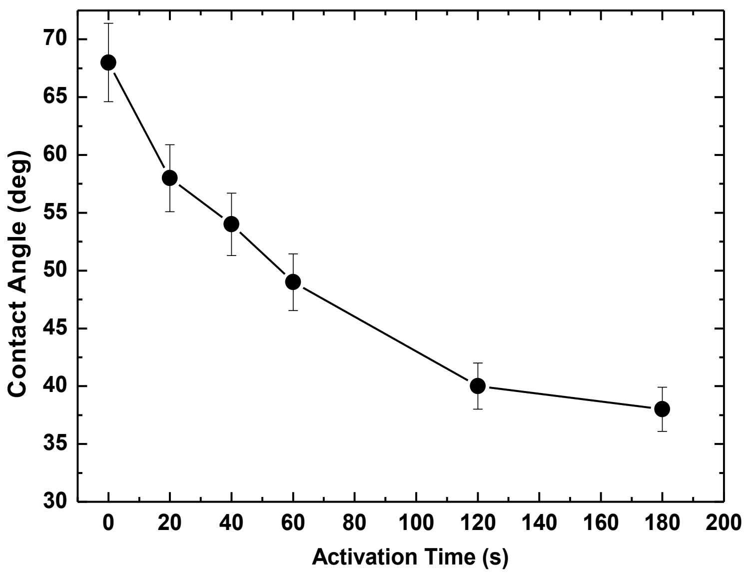


Figure 5. Contact angle of water on beech wood surface modified by RF discharge plasma vs. activation time.

CONCLUSION

The surface roughness of RF plasma-treated beech wood, as analysed by AFM, slightly decreased. Nano indentation measurements confirmed, that ablation processes induced during the modification of beech wood by RF plasma did not significantly alter the roughness of the beech wood surface. The content of oxygen and nitrogen measured during the RF plasma treatment of beech wood increased. Conversely, the amount of carbon decreased. The content of COOH, C–O and C=O groups during treatment by RF plasma significantly increased. The contact angle of water decreased with the activation time of the RF plasma treatment and showed a steep decrease from 66^{o} deg (pristine beech wood) to 40^{o} after 120 s of activation by RF plasma in air.

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Streszczenie: *Modyfikacja drewna za pomocą plazmy RF*. W ramach badań wykorzystano plazmę niskotemperaturową wtrwarzaną w generatorach radiowych częstotliwości (plazma RF) do modyfikacji powierzchni drewna pod kątem poprawy jego sklejalności. Wstępna obróbka powierzchni drewna za pomocą plazmy RF może być wykorzystana przy różnych jego zastosowaniach, głównie ze względu na wysoką wydajność i niski koszt procesu modyfikacji. Obróbka drewna plazmą RF wywołała efekt starzenia jego powierzchni. Modyfikacja miała charakter trwały, powierzchnia drewna nie odzyskała swoich początkowych właściwości hydrofobowych. Kąt zwilżania powierzchni drewna wodą zmniejszał się wraz z wydłużeniem czasu aktywacji plazmą RF.

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