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STUDY OF WOOD SURFACE PRE-TREATMENT BY RADIO-FREQUENCY DISCHARGE PLASMA

*An investigation was made of wood of the species oak (*Quercus petraea*), beech (*Fagus sylvatica* L.), maple (*Acer pseudoplatanus*) and ash (*Fraxinus excelsior*) pre-treated using radio-frequency (RF) plasma in air at reduced pressure. Physical and chemical changes for all of the wood species were determined using measurements of water contact angles and FTIR-ATR spectroscopy. The results confirmed an increase in the wood's hydrophilicity/polarity in all cases, caused by an increase in –OH group concentration due to irradiation by RF plasma. The content of oxygen-containing functional groups after treatment by RF plasma significantly increased, and the water contact angles were diminished. FTIR-ATR spectroscopy confirmed that RF plasma modification of the surfaces of all investigated wood samples led to certain changes, which were also dependent on the time of plasma exposure.*

Keywords: FTIR-ATR, RF plasma treatment, wood surface, water contact angle, hydrophilicity

Introduction

Low-temperature plasma has been suggested as an appropriate procedure for the hydrophilization of polymeric surfaces [Novák et al. 2012]. Due to the plasma treatment, the surface free energy of wood is increased as a result of the generation of polar functional groups on the treated surface, thus making the surface of wood more hydrophilic [Kamdern et al. 2000]. The use of radio-

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frequency (RF) discharge plasma at reduced pressure is currently an efficient method for surface treatment and the obtaining of adhesive properties of wood, and is considered an ecologically friendly (“green”) method. To enable a wide range of industrial uses, wood species must offer a large set of different surface characteristics, including polarity, dyeability, scratch resistance, tailored adhesive properties, antibacterial resistance, etc. [Bente et al. 2004; Wolkenhauer et al. 2009; Acda et al. 2012]. Nanoscale dimensional changes have been achieved in plasma-treated wood, while maintaining the desirable material properties. The enhancement of wood surface hydrophilicity is a necessary condition to promote better adhesion with water-based adhesives and coatings, and this is currently the subject of research [Frihart 2005; Odrášková et al. 2008; Moghadamzadeh et al. 2011; Reinprecht and Šomšák 2015].

There are two reasons why discharge plasma can be successfully used for the surface modification of wood [Odrášková et al. 2008]. Firstly, discharge plasma in air significantly increases the hydrophilicity of wood, because various polar groups are formed (hydroxyl, carbonyl, carboxyl, etc.), and the wood macromolecules are also cross-linked (up to a few microns), which leads to an increase in scratch resistance and to an improvement in the barrier properties of the wood material. The second reason for the use of plasma is an increase in adhesion in adhesive joints between polymeric adhesives and the wood substrate, due to an increase in the wood’s wettability, which is important for industrial applications. Low-temperature plasma represents a mixture of various excited particles, i.e. ions, atoms, electrons, and radicals with a low degree of ionization and little penetrating energy, but plasma particles have sufficient levels of energy to break chemical bonds on the wood substrate [Olaru et al. 2005]. The impact of the treatment of wood by discharge plasma is limited to a depth of 100 nanometres; there is no effect on the bulk properties of the material [Odrášková et al. 2008]. The increased surface polarity, due to oxidation reactions during the modification of wood by RF plasma, improves its wettability and hydrophilicity [Müller et al. 2009; Ciolacu et al. 2011]. Thermo-oxidative stability of modified materials can be tested, for example, by differential scanning calorimetry (DSC). This method is based on determination of the end of the induction period or the beginning of the main oxidation process [Šimon and Kolman 2001; Šimon 2006]. Wettability assists in establishing molecular scale contact with the wood surface and is critical to the obtaining of strong adhesion at the adhesive/wood interface [Kúdela et al. 2017].

The aim of this study was to investigate the surface and chemical properties of selected species of wood following surface modification by radio-frequency plasma in air.

Materials and methods

Samples of wood from oak (*Quercus petraea*), beech (*Fagus sylvatica* L.), maple (*Acer pseudoplatanus*) and ash (*Fraxinus excelsior*) with dimensions $50 \times 15 \times 5$ mm (Technical University in Zvolen, Slovakia) and a moisture content of 8% were pre-treated using RF plasma in the air at a pressure of 100 Pa.

The physical and chemical changes in all of the wood species were observed using measurements of water contact angles obtained by means of a contact angle meter, and using an FTIR-ATR device.

RF plasma modification

The surface of the wood was modified by RF discharge plasma. The modification of wood by capacitive coupled RF plasma was performed in a laboratory RF plasma reactor (fig. 1) working at a reduced pressure of 100 Pa, consisting of two 240 mm brass parallel circular electrodes with a symmetrical arrangement, 10 mm thick, between which RF plasma was created.

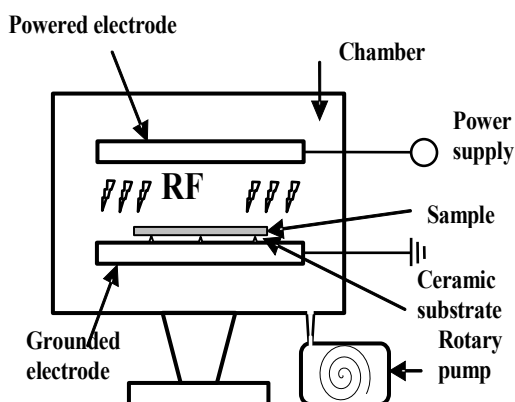


Fig. 1. Diagram of RF plasma source

The two electrodes of the RF plasma reactor are contained in a closed stainless steel vacuum cylinder. One is powered, and the other is grounded together with the steel cylinder. The RF plasma reactor has a voltage of 2 kV, a frequency of 13.56 MHz and a maximum current intensity of 0.6 mA. The maximum power of the RF plasma source is 1200 W. The wood samples were modified by RF plasma at a power of 350 W.

Measurement methods

The surface energy of wood was measured by the determination of contact angles (θ) with re-distilled water as the testing liquid [Odráškova et al. 2008].

The drops of testing liquid ($V = 20 \mu\text{l}$) were placed on the wood surface with a micropipette (Biohit, Finland), and the graph of the function $\theta = f(t)$ was extrapolated to $t = 0$. Water contact angle measurements were taken using a professional SEE (Surface Energy Evaluation) system device coupled to a web camera (Advex, Czech Republic) and required PC software. The measurements of contact angles were repeated 12 times, and the arithmetic mean and standard deviation of the measurements were taken for analysis.

A hardness value was determined for each type of wood according to the Brinell hardness (BH) test.

Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance (FTIR-ATR) measurements were performed with a Nicolet 8700 FTIR 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 water contact angle on the investigated wood surfaces diminished with an increase in the time of modification by RF discharge plasma, and exhibited a steep decrease from 74° (pristine oak wood) to 45° after activation of oak wood by RF plasma in the air for 60 s (fig. 2). The decrease in the water contact angle can be explained by an increase in the hydrophilicity of the investigated wood surfaces during pre-treatment by RF plasma in air. The hydrophilicity of the wood surface depends on the formation of polar oxygenic functional groups during RF plasma modification. At saturation of the wood surface with polar groups (after 60 s of plasma treatment), the hydrophilicity stabilized. The effectiveness of modification of the wood surface by RF plasma was lower in the case of ash wood, for which the effect on the water contact angle was smaller than in the case of oak, beech and maple.

The aging of RF plasma-treated wood species is illustrated in figure 3. During aging after modification by RF plasma, the water contact angle of the modified wood surfaces increased rapidly for two days, after which the aging process was slower. The increase in the water contact angle over the total aging time was smaller in the case of ash wood than in the case of oak, beech and maple. The water contact angle of RF plasma-treated beech wood increased from 42° to 64° over 21 days of aging, a rise of 52.4%.

In general the spectrum of any kind of wood is a mixed spectrum (composition) of cellulose and lignin with characteristic peaks corresponding to O–H bonds (with a maximum at about 3400 cm^{-1}) and fingerprints assigned to the $-\text{C}-\text{O}-\text{C}-$, $-\text{COO}$ and $-\text{CH}_2-$ bonds typical for polysaccharides. Moreover, the peak at 898 cm^{-1} corresponding to glycosidic linkages appears for each of them as a typical spectral band [Ciolacu et al. 2011]. So-called normalized

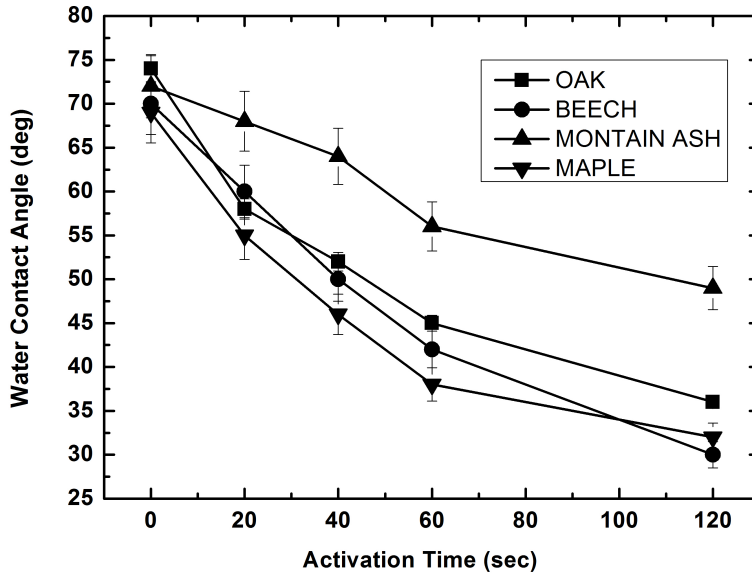


Fig. 2. Water contact angle of RF plasma-treated wood species vs. plasma activation time

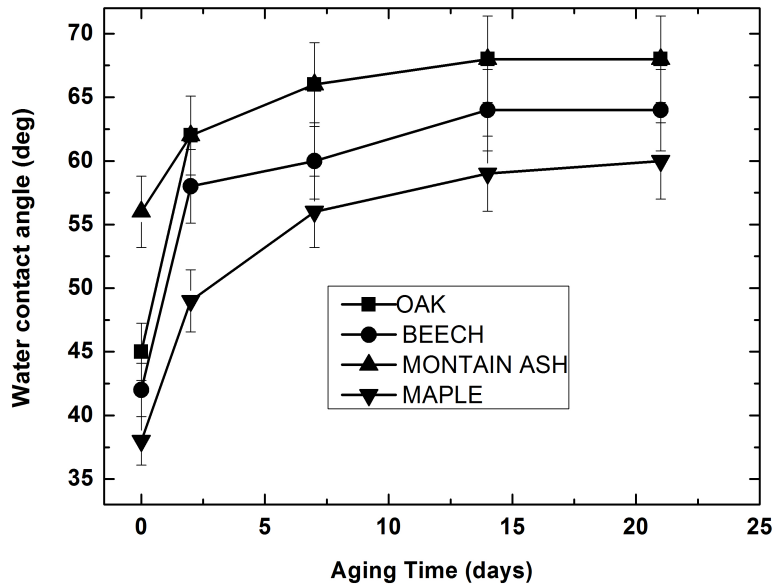


Fig. 3. Water contact angle of RF plasma-treated wood species vs. aging time

spectra, i.e. FTIR-ATR spectra modified by multiplication by a factor chosen to allow a common Y-axis for better readability, are presented in figures 4-7. Thus small changes in the shapes of the absorption bands assigned to ->C-H and

-)C–O–C(- bonds, which confirmed changes on the surfaces of the wood samples, are more easily better observed. However, since the spectral band was composed of more parts, a different procedure was chosen to quantify these changes. The ratios of integrated intensities of spectral bands assigned to oxygen-bonding groups (with the majority contribution of –OH groups, with a maximum at 3400 cm^{-1}) and integrated intensities of the spectral band assigned to $(-\text{CH}_2-)_{\text{sym}}$ with a peak at 2985 cm^{-1} were determined. However, this represents only semi-quantitative information, e.g. providing confirmation or exclusion of the impact of RF plasma treatment on the wood surface. The ratios of integrated intensities $P(-\text{OH})/P(-\text{CH}_2-)_{\text{sym}}$, where the intensity of symmetrical stretching vibrations of $-\text{CH}_2-$ bonds was chosen as an internal standard, are presented in table 1. It was assumed that RF plasma treatment did not affect $-\text{CH}_2-$ groups.

Figures 4, 5, 6, and 7 show the increased ratio of specified intensities for RF plasma-treated samples of all investigated wood species compared with untreated samples. For maple wood it may be concluded that the values of this ratio correlate with the time of exposure to RF plasma. The largest increase was observed in the case of beech wood (from a value of 7.433 for untreated beech wood to 22.986 after 120 seconds of RF plasma treatment). The ratio $P(-\text{OH})/P(-\text{CH}_2-)_{\text{sym}}$ for the untreated samples of woods ranges from 5.948 to 7.433, indicating similar hydrophilicity, and accordingly content of oxygen-bonding groups, on the surfaces of all types of wood investigated before any plasma treatment. The values of the ratio for ash wood, with a hardness of 4.0 BH, were very similar for all time regimes, which may be due to the fact that the ash was the hardest of the evaluated wood species, meaning that RF plasma treatment in this case was not so effective. Indeed, the baseline for the ratio was the lowest in the case of ash wood. It should be noted, however, that the hardness values of the materials are not dependent on the type of surface, in this case on the porosity, which may be a reason why RF plasma treatment is more effective in some cases and less in others. It can be concluded from the FTIR-ATR spectroscopy results that RF plasma treatment caused some changes on the surfaces of all investigated species of wood. These changes were dependent on the plasma activation time in the case of maple wood. This trend was not completely proven for the other species of wood, but it may be observed that there was an increased content of hydrophilic groups in the plasma-treated samples compared with the untreated samples. The findings of FTIR-ATR spectroscopy may also be supplemented by the results of water contact angle measurements.

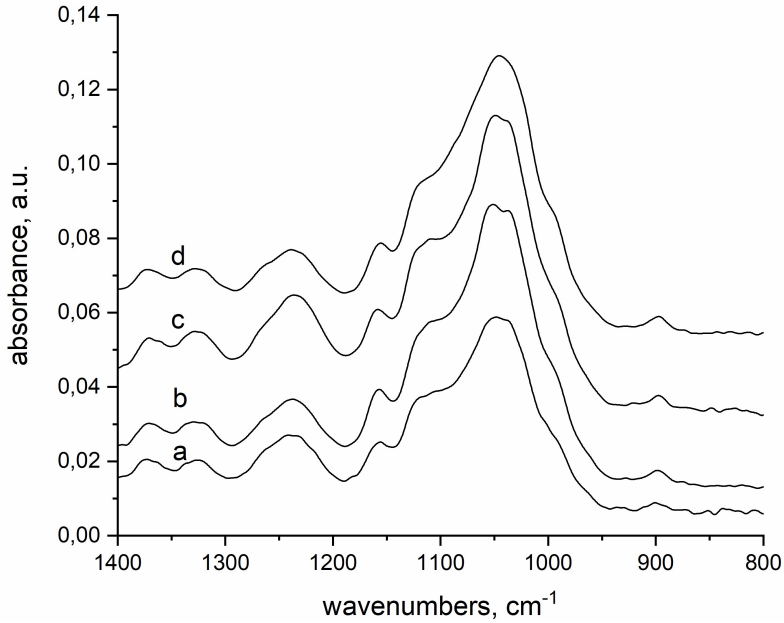


Fig. 4. FTIR-ATR spectra of oak wood surface untreated by RF plasma (a) and following RF plasma treatment for: 20 s (b), 60 s (c) and 120 s (d)

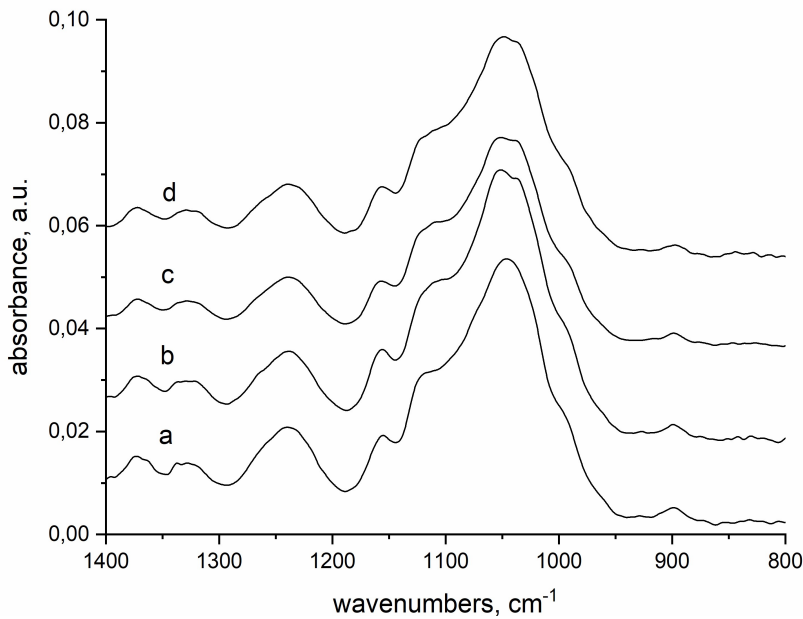


Fig. 5. FTIR-ATR spectra of beech wood surface untreated by RF plasma (a) and following RF plasma treatment for: 20 s (b), 60 s (c) and 120 s (d)

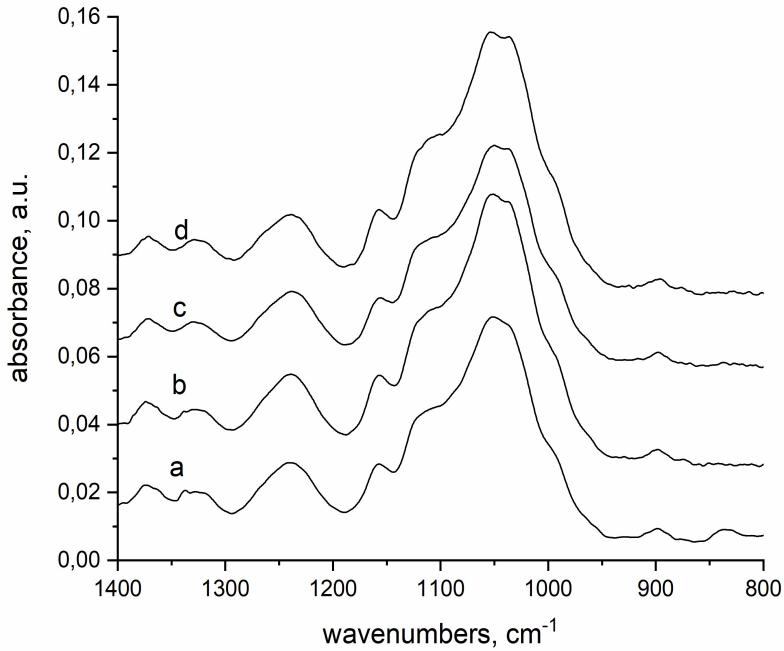


Fig. 6. FTIR-ATR spectra of maple wood surface untreated by RF plasma (a) and following RF plasma treatment for: 20 s (b), 60 s (c) and 120 s (d)

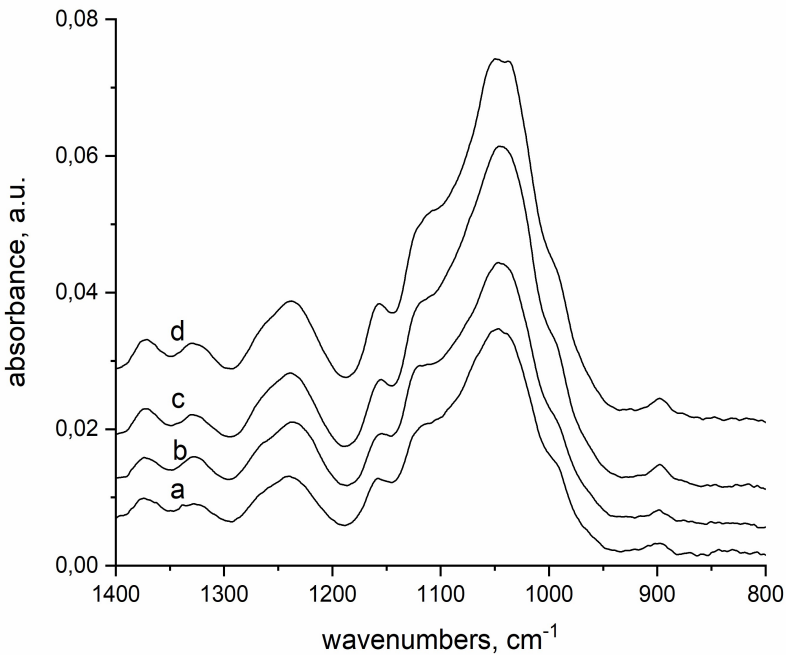


Fig. 7. FTIR-ATR spectra of ash wood surface untreated by RF plasma (a) and following RF plasma treatment for: 20 s (b), 60 s (c) and 120 s (d)

Table 1. Integrated intensities (P) of selected spectral bands on the FTIR-ATR spectra for surfaces of wood species (oak, beech, maple and ash) pre-treated by RF discharge plasma

Type of wood / Brinell hardness / RF plasma activation time	Integrated intensities of analyzed spectral bands (internal standard, polar oxygen-containing groups, combined integrated intensities for oxygen-bonding groups incl. –OH stretching vibrations)		Final ratio
	P (2895 cm ⁻¹ , –CH ₂ – sym. stretching vibrations)	P (3400 cm ⁻¹ , –OH stretching vibration)	P(Oxy groups)/P(–CH ₂ –) _{sym}
Oak, 3.7 BH			
Untreated	0.593	4.017	6.863
20 s plasma	0.563	5.376	9.549
60 s plasma	0.508	6.334	12.469
120 s plasma	0.440	7.622	17.414
Beech, 3.8 BH			
Untreated	0.552	4.103	7.433
20 s plasma	0.364	5.086	13.973
60 s plasma	0.306	6.311	20.624
120 s plasma	0.284	6.528	22.986
Maple, 3.0 BH			
Untreated	0.763	4.538	5.948
20 s plasma	0.538	6.141	11.414
60 s plasma	0.483	6.784	14.046
120 s plasma	0.430	7.293	16.960
Ash, 4.0 BH			
Untreated	0.643	4.387	6.823
20 s plasma	0.597	6.472	10.841
60 s plasma	0.523	7.015	13.413
120 s plasma	0.540	7.151	13.243

Conclusions

The water contact angle of the investigated wood species treated by RF plasma in air decreased with activation time from 74° to 30°. During aging of the wood samples after the plasma pre-treatment the water contact angle increased rapidly for two days, and subsequently more slowly. The water contact angle values of the four wood species exhibited a steep decrease after activation by RF plasma in air. The plasma-treated wood surfaces should subsequently undergo procedures such as bonding, painting, etc. within two days of modification by plasma.

FTIR-ATR spectra confirmed the increase in polarity of the selected wood species as a result of treatment with RF discharge plasma in air, due to the increase in the quantity of –OH groups. The concentration of oxygen-containing groups on the wood surface markedly increased after treatment by RF plasma.

Based on the FTIR-ATR results it may be observed that there is an increased content of hydrophilic groups on the surfaces of the plasma-treated wood samples compared with the untreated samples.

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