WOOD SURFACE MODIFICATION BY DIELECTRIC BARRIER DISCHARGES AT ATMOSPHERIC PRESSURE

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1. Introduction

Like other biological materials, wood is susceptible to environmental degradation[1]. Interaction of wood with water can lead to dimensional instability and accelerated bio as well as weathering degradation. Because of this, the surface of wood has to be protected to prolong its durability. Majority of paint and wood adhesives are water–based. Water wetting is an important parameter for bond formation. In general wood exhibited a good wettability by water, nevertheless some woods of high lignin content (like oak) are hard to wet. A chemical treatment of the wood surface that promotes better wettability or provides new bonding sites, should improve adhesive bond performance. The same effect can be achieved using the plasma treatment. Majority of tests have been performed at low pressure, however these processes are very cost consuming[2]. This constraint can be overcome by the treatment of plasma generated at atmospheric pressure[3], which effect on improving the wetting and adhesion properties of various polymer materials have been extensively studied for last 10 years. The surface activation was carried out using coplanar barrier discharge[5] in the ambient air to obtain wettable surface suitable for easy painting. Our results in activating the hydrophobic oak surface will be presented in this paper.

By choosing a suitable composition of discharge gas, the hydrophobic surface properties of wood can be obtained too[4]. In presented study, plasma assisted deposition of hydrophobic coatings was performed directly on the surface of poplar veneer by surface barrier discharges at atmospheric pressure from the mixture of nitrogen containing HMDSO vapors. We will present these results as well.

2. Experimental

For hydrophobization study the samples of poplar veneer with dimension 700 × 130 × 0.5 mm were used. The sample surface was sanded by sandpaper of 150-grit.

Plasma activation study (creating a hydrophilic surface) was performed on oak heartwood samples with the dimensions of 50 × 15 × 5 mm. The oak was chosen because of its known low surface energy (36.1 mJ m^{-2}) resulting in poor water wettability.

The deposition of thin hydrophobic layer was carried out by surface barrier discharge (SBD) at atmospheric pressure[6]. The surface discharge was created on the surface of the mica dielectric plate, fully covered with metal electrode on one side. The opposite side of the mica plate was in contact with metal electrode consisting of 11 connected rotating rods of 9 mm. The rods were 10 cm long. The whole arrangement was placed in deposition chamber. The SBD electrodes were energized by 5 kHz sinusoidal high voltage generator LIFETECH VF 700. The poplar veneer strip was drawn with controlled speed through the chamber between the metal electrodes and the dielectric mica plate. The discharge appeared along the substrate surface in the decreasing initial electric field from the side of the rod metal electrodes. The surface power density was kept at 1.1 W cm^{-2} in all cases. Configuration of the reactor is shown in Fig. 1.

The layers were deposited from mixture of nitrogen with different amount of hexamethyldisiloxane (HMDSO) vapors. The flow rate of nitrogen was kept at 6 l min^{-1} in this study and the HMDSO flow rate varied between 0.06 and 0.4 g min^{-1} in order to optimize the coating properties. Plasma activation of wooden samples was done by the coplanar surface barrier

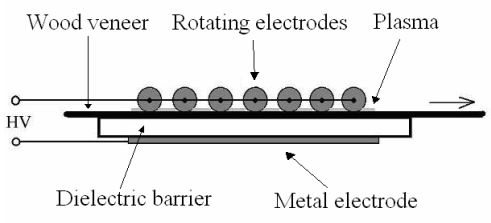

Fig. 1. **Scheme of deposition reactor based on Surface Barrier Discharge**

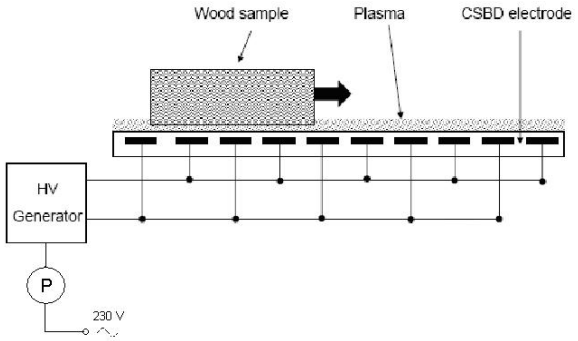

Fig. 2. **Scheme of the reactor based on Coplanar Surface Barrier Discharge**

discharge[5]. The coplanar surface barrier discharge electrodes consisting of 15 pairs of silver strip electrode embedded 0.5 mm below the surface of 96 % Al_2O_3 ceramics were energized by 14 kHz sinusoidal voltage, supplied by HV generator LIFETECH VF 700. The mutual distance of the 200 mm long and 2 mm wide silver strip electrodes was 1 mm. The electrode system was mounted inside the closed reactor chamber equipped with a moving sample holder (Fig. 2).

The surface of oak samples was sanded by sandpaper of 150-grit before the surface energy measurement and by 100-grit before the water uptake time measurement. Wood samples were mounted to the moving sample holder and conveyed to the intimate contact with the plasma generated above the ceramics surface. Plasma activation was done in ambient air with an average plasma power density 2.2 W cm^{-2} and exposure time of 5 s. The wood moisture content was within the range of 7–8 % in all cases.

The surface properties of plasma treated and untreated wooden samples were investigated by means of the sessile drop technique using the Surface Energy Evaluation System (SEE System, http://www.seesystems.wz.cz). The contact angles were measured directly from the images of the solid/liquid meniscus of a liquid drop set on a solid surface taken with CCD camera. The value of wood total surface free energy γ_s and its disperse γ_s^d and polar γ_s^p components was calculated by means of Owens-Wendt method[6] expressed as:

$$\left(1+\cos\Theta\right)\gamma_L = 2\sqrt{\gamma_L^d\gamma_S^d} + \sqrt{\gamma_L^p\gamma_S^p}$$

were Θ is the contact angle of the test liquid with the sample, γ_L is total surface energy of the test liquid, γ_L^d is dispersion component and γ_L^p is polar component of the testing liquid. γ_S^p and γ_S^d are dispersive and polar components of the surface energy of the tested sample. In the case of characterization of hydrophobic coatings deposited in SBD the contact angle was measured with following testing liquids: water, glycerol, ethylene glycol, formamide, diiodomethane, α-bromonaphtalene. In the case of characterization of plasma activated samples the contact angle was measured with water, diiodomethane and α-bromonaphtalene. Water is a representative of polar liquid, diiodomethane and α-bromonaphtalene are non-polar testing liquids. Two combinations of water + diiodomethane and water +α-bromonaphtalene were used as a test liquid pairs for evaluation of surface free energy of activated samples using Owens-Wendt method.

The water uptake time was measured as the time from the impact of the droplet to its complete penetration into the wood surface (no optical reflection can be seen). For this test one half of each wooden sample surface was activated by plasma while the second half was left untreated. The water droplet of 50 μl was put on the plasma activated part of sample and second one on untreated part of oak surface. According to the method described[7] the uptake time was evaluated for 15 oak samples.

3. Results

Highly hydrophobic thin layers were deposited on the poplar veneer surface in order to protect it against water penetration. Organosilicon monomer (HMDSO) mixed with nitrogen was used as a working gas during the plasma deposition to create protective hydrophobic layer. Water droplet on untreated poplar veneer surface is shown in Fig. 3. After the plasma deposition the contact angle increased from 63° to 120° which proves the hydrophobic nature of deposited layer (see Fig. 4). The concentration of monomer and also deposition time were varied to obtain optimal deposition conditions and also surface properties. Fig. 5 shows the total surface free energy as a function flow rate of HMDSO. Total surface free energy exponentially decreases with increasing monomer flow rate. The most hydrophobic layer were deposited when the deposition time was 120 s. Fig. 6 shows the total surface energy and its polar and dispersion part as a function flow rate of HMDSO. In this case the deposition time was 42 s. The dispersion component quickly decreases with the increasing flow rates HMDSO, however polar part remains almost constant. Similar behavior was obtained also for samples with different deposition times.

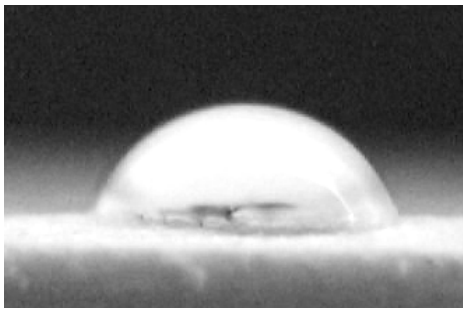

Fig. 3. **Water droplet on the surface untreated poplar veneer**

The results of plasma activated oak surfaces are summarized in Tab. I. The value of total free surface energy increased from 40 to 74 mJ m^{-2}, mainly due to the rise of its polar component. The results of water uptake time measurement are shown in Tab. II.

The uptake time reduced from 675.8 to 61.5 s after the plasma treatment, the mean relative reduction of uptake time was 88 ± 7 %. Our result is in the same order of magnitude as those declared[7]. Fig. 7 shows a plane view of the treated (left sample) and untreated (right sample) oak samples 10 s after the dropping of water droplet on sample surface. Water wets

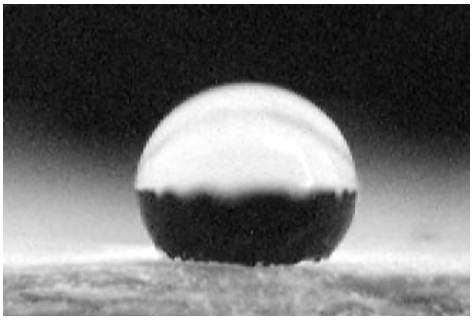

Fig. 4. **Water droplet on the poplar veneer after coating**

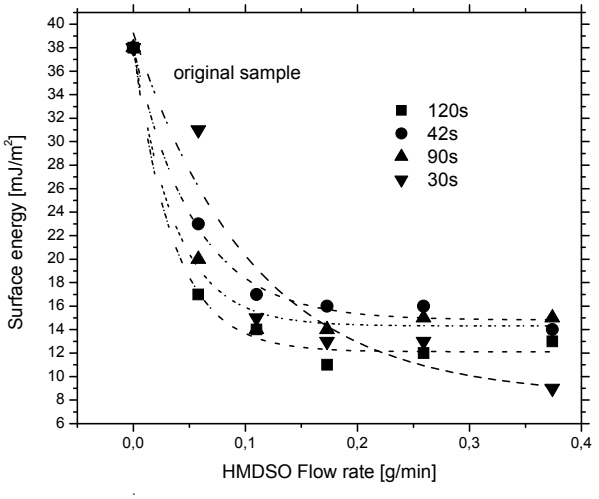

Fig. 5. **Total surface free energy as a function of HMDSO flow rate. Flow rate of nitrogen 6 l min^{-1} was kept constant in all cases**

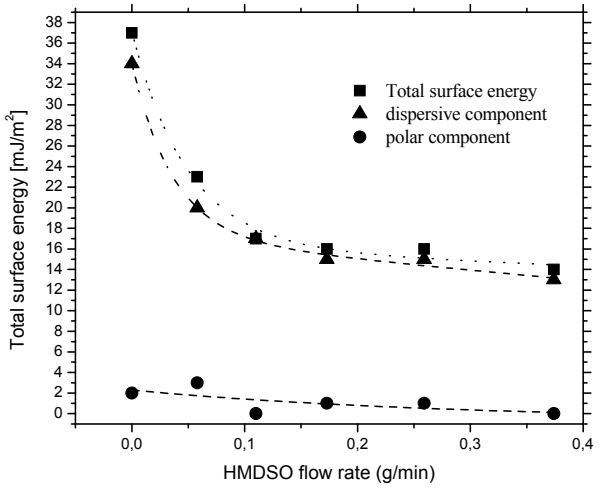

Fig. 6. **Total surface free energy γ^{tot} and its dispersive γ^d and polar γ^p parts a function of HMDSO flow rate. Flow rate of nitrogen 6 l min^{-1} was kept constant in all cases**

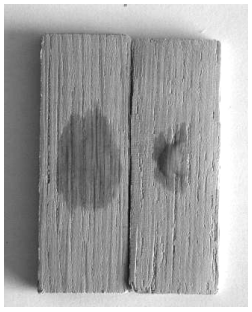

Fig. 7. **Plane view on plasma treated (left) and untreated (right) oak samples 10 s after placing 50 μl water droplet on the surface**

Table I
Total surface free energy γ^{tot} and its dispersive γ^d and polar γ^p parts of oak surface (in radial section) before and after the plasma treatment

Testing liquid	Water and diiodomethane		Water and α-bromonaphtalene	
[mJ m^{-2}]	original	activation	original	activation
γ^{tot}	40.71	74.26	42.36	73.80
γ^d	39.56	45.40	41.40	44.43
γ^p	1.15	28.26	0.96	29.37

Table II
Water uptake time of plasma activated (T_A) and untreated (T_0) oak in radial section

	Untreated oak T_0 [s]	Treated oak T_A [s]	$(1-T_A/T_0)100$ % [%]
1	317	56	82
2	1850	90	95
3	606	45	93
4	231	42	82
5	949	75	92
6	379	61	84
7	1072	90	92
8	1190	41	97
9	154	45	70
10	1421	61	96
11	1078	84	92
12	333	54	84
13	463	68	85
14	443	47	89
15	501	65	87
Mean	732.6	61.5	88 ± 7

preferentially in direction of the surface capillaries.

Comparing the energy consumption[7], system based on volume barrier discharge needs 0.1 kWh m^{-2}, however system based on DCSBD, needed only about 0.03 kWh m^{-2} of wood surface. The system based on DCSBD offers a considerably better efficiency. Moreover the plasma treatment in DCSBD is completely independent on the thickness and electrical conductivity of the treated wood material.

Highly hydrophobic plasma polymer coatings were deposited on the wood substrate in surface barrier discharge from the mixture of HMDSO monomer with nitrogen. The total surface free energy of sample decreased from 37 mJ m^{-2} before coating wood to about 12–17 mJ m^{-2} (after the plasma deposition).

The plasma activation of wooden surfaces in diffuse surface barrier discharge was tested. The total surface energy increased from 40 to 74 mJ m^{-2} after plasma treatment.

The plasma activation of wood in DCSBD promotes a better adhesion and efficiency then competitive systems.

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([a] Univerzita Komenského, Bratislava, Slovak Republic; [b] Masarykova Univerzita, Brno, Czech Republic): **Wood Surface Modification by Dielectric Barrier Discharges at Atmospheric Pressure**

The effect of plasma treatment at atmospheric pressure on surface properties of wooden samples is investigated in this work. Plasma activation of wooden surface was studied in diffuse coplanar surface barrier discharge created in air to obtain wettable surface. Plasma deposition of hydrophobic coatings directly on the surface of wooden materials using surface barrier discharge created in pure nitrogen with small admixture of hexamethyldisiloxane was investigated too. Surface properties of plasma treated wooden samples were studied using the sessile droplet technique to identify surface free energy of treated and untreated samples.