Water-Repellent Coatings on Wood Surfaces Generated by a Dielectric Barrier Discharge Plasma Jet at Atmospheric Pressure

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ABSTRACT

In this study the feasibility of plasma polymerisation on wooden substrates at atmospheric pressure was investigated. An atmospheric-pressure plasma jet using hexamethyldisiloxane as precursor and air as process gas was used for thin layer deposition. Treatment parameters for the layer deposition were investigated, as well as the layer topography and chemical composition. Atomic force microscopy revealed a closed surface layer consisting of silicon, oxygen, carbon and hydrogen that exhibited low water permeability.

INTRODUCTION

Techniques such as painting and lacquering are used to coat wood surfaces for aesthetic reasons and to protect against water penetration and excessive wood moisture content, thus preventing premature biological and weathering degradation. A less common technique for wood protection is electrical gas or plasma discharge (Janzen 1992). Plasmas are applied in a wide range of surface modification and thin layer deposition techniques to alter the surface characteristics of solids such as metals, glasses and plastics (Hippler *et al.* 2001, Inagaki 1996). This approach is also attracting research interest for surface modification of wood and wood-based materials (Podgorski *et al.* 2000, Klarhöfer *et al.* 2005, Evans *et al.* 2007, Topala and Dumitrascu 2007, Wolkenhauer *et al.* 2008a–c, 2009, Custódio *et al.* 2009). Plasma-based surface modification is environmentally friendly and modification is confined to the outermost surface layer and does not affect the bulk properties. It can be used to increase hydrophilicity and wettability for enhanced adhesion or to create and deposit special surface layers using suitable process gases, such as plastic-, silica- or even diamond-like carbon layers on various surfaces (Hippler *et al.* 2001, PSE 2006). Hydrophobisation with hexamethyldisiloxane (HMDSO) ($Si_2OC_6H_{18}$) by plasma polymerisation has been used to achieve water-repellent wood surfaces (Denes *et al.* 1999, Mahlberg *et al.* 1998, Odrásková *et al.* 2007). Many studies have investigated plasma-based polymerisation under vacuum conditions, which requires expensive vacuum equipment, but surface treatment can be conducted at atmospheric pressure using a dielectric barrier discharge (Kogelschatz 2003). This plasma set-up does not require vacuum conditions, is more effective because of the higher pressure and is well suited for the creation and deposition of thin hydrophobic layers on wood surfaces (Rehn *et al.* 2003, Bente *et al.* 2004, Odrásková *et al.* 2007, 2008a). In contrast to Denes *et al.* (1999) and Mahlberg *et al.* (1998), who conducted plasma treatment at low pressure, and Odrásková *et al.* (2007, 2008a,b), who used a diffuse coplanar surface barrier discharge, which requires a small discharge gap of 0.3 mm, in the present study a plasma jet was used to create a HMDSO-containing plasma at atmospheric pressure. This set-up combines the advantages of atmospheric pressure and a certain degree of independence from the surface profile, substrate material and thickness, and is therefore well suited for the deposition of thin surface layers on wood. To assess the water repellency and permeability of layers deposited on wood surfaces, water penetration tests were conducted. The topography of layers deposited on wood and microscope slides was analysed using an atomic force microscope (AFM). To determine the elemental and chemical composition of deposited layers, glass substrates were plasma coated and CHN analysis and Fourier-transform infrared (FT-IR) spectroscopy were carried out.

EXPERIMENTAL

For plasma deposition of thin surface layers, beech (*Fagus sylvatica*) was sawn into pieces of 100×20×3 mm^3 (radial cut), sanded with abrasive paper (P240) and stored for 24 h in a climate chamber at 20°C and 50% relative humidity prior to plasma treatment. For AFM imaging, CHN analysis and FT-IR spectroscopy, microscope slides used as substrates were cleaned with acetone directly before plasma treatment. Figure 1 shows the plasma jet used, which consisted of two rectangular electrodes insulated by Al_2O_3 to form a rectangular discharge gap of 2×20×160 mm^3, which was sealed by two fused quartz sheets. One electrode was grounded and the other was connected to an alternating high-voltage pulse generator (f=17 kHz, pulse length 2 μs). The process gas was blown through the discharge gap towards the sample to be coated. The distance between the sample and the jet outlet was 2 mm and the treatment time for all experiments was t_t=18 s. During plasma treatment, gas temperatures of 100°C were measured using a fibre optical thermometer (FTI-10, FISO Technologies). The process gas consisted of argon (purity >99.99%) as carrier gas fed through liquid HMDSO as the precursor. HMDSO-loaded argon was then mixed with synthetic air (nitrogen/oxygen 79.5:20.5, purity >99.99%). The electrical power dissipated in the plasma and the air/Ar ratio were varied to investigate their impact on the deposited layers. To assess the water permeability of the deposited layers, a 50-μl water droplet was applied to the plasma-coated beech surface and its penetration time into the wood was measured (Kress *et al.* 1999, Bente *et al*. 2004). The water penetration time was taken as the time from impact of the droplet to complete penetration into the wood surface. To minimise evaporation of the water droplet, the test was conducted at relative humidity of approximately 100%. To determine the elemental composition of the layer, a CHN analyser (Heräus CHN-Rapid) was used. Silicon was detected photometrically using a Perkin Elmer Lambda 2 spectrophotometer at the Institute of Inorganic Chemistry, Georg-August University, Göttingen.

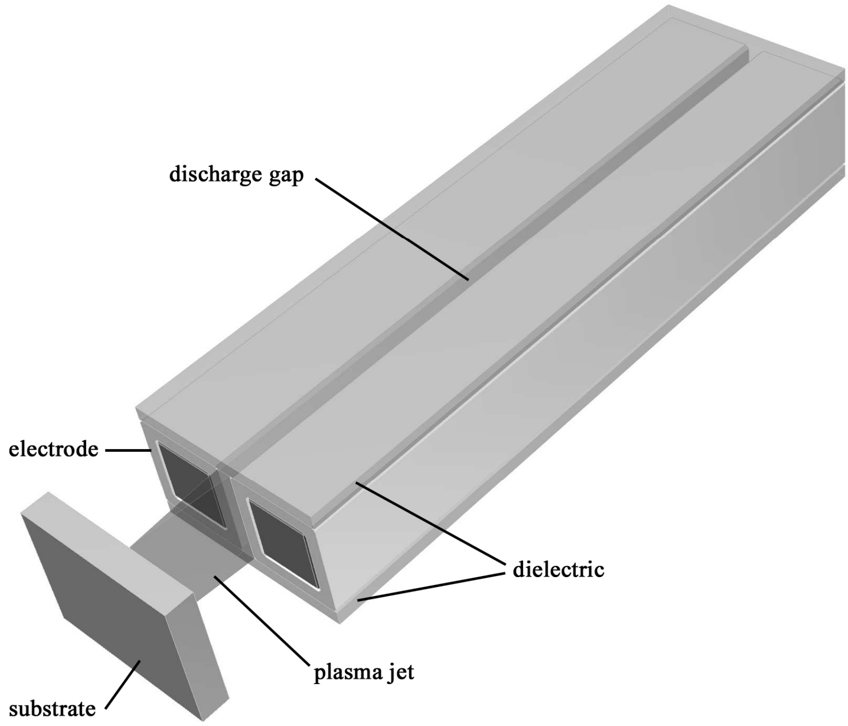

Figure 1: Schematic sketch of the plasma jet used

FT-IR spectroscopic measurements of the deposited layer were made on a Perkin Elmer FT-IR spectrometer using the KBr technique in transmittance mode. Data were collected for 100 scans at a resolution of 4 cm^{-1}. An Easyscan 2 (Nanosurf AG) AFM equipped with Nanosurf Easyscan 2 (v-1.8.0) software was used to examine the surface topography of the deposited layers. Measurements were carried out in static force mode at a tip force of 10 nN.

RESULTS AND DISCUSSION

To assess the effect of the electrical power dissipated in the plasma on the layer performance and to determine suitable parameters for further investigations, water permeability tests were performed on layers deposited on beech. For this purpose three different power levels were chosen: 67 W, which is the minimum energy required for plasma ignition, 102 W, which is the highest level of the power source used, and 81 W. For this test the air/Ar ratio was constant at 5:1. Five droplets for each sample were applied and the mean and standard deviation were calculated. Figure 2 shows the water permeability results for layers generated at different electrical power. It is clear that the water penetration time increased from 70 to 120 to 290 min when the power was increased from 67 to 81 to 102 W, respectively, whereas the uncoated control had the shortest water penetration time. Creatore *et al.* (2002) and Vautrin-Ul *et al.* (2002) reported an increase in layer density and a decrease in voids in the layer structure with increasing power, making the layer more suitable as a diffusion barrier. On the basis of these results, subsequent tests were conducted at the highest power level of 102 W. Figure 2 shows water permeability results for tests carried out at a constant power level of 102 W and different air/Ar ratios. The water penetration time increases from 60 to 290 and 480 min as the volume flow ratio increased to 10:1. A further increase in flow ratio to 15:1 led to a decrease in water penetration time to 120 min. Similar results were reported by Odrásková *et al.* (2007) for varying nitrogen/HMDSO-loaded nitrogen ratios. Wang *et al.* (2003) identified an optimum mixing ratio for HMDSO and oxygen that yielded the best layer characteristics. Since the best water permeability results were obtained for a power level of 102 W and an air/Ar ratio of 10:1, further investigations were conducted using these parameters.

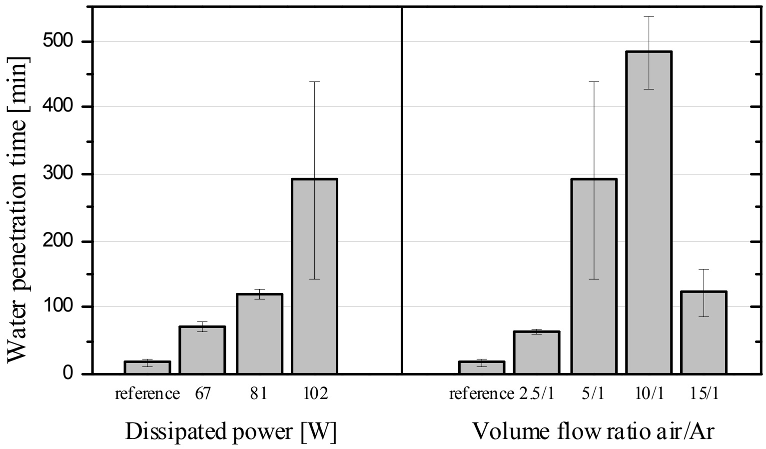

Figure 2: Water penetration time for different power levels and air/Ar ratios

To investigate the surface topography of the deposited layers, AFM imaging was carried out. Figure 3 shows AFM images of uncoated and plasma-coated beech. The microstructure of the wood surface (Figure 3 left) appears to be completely covered by the deposited layer (Figure 3 right), whereas the macrostructure is still visible. A notable feature is the nodule-like fine structure of the layer, which was also found by Denes *et al.* (1999) and Vautrin-Ul *et al.* (2002).

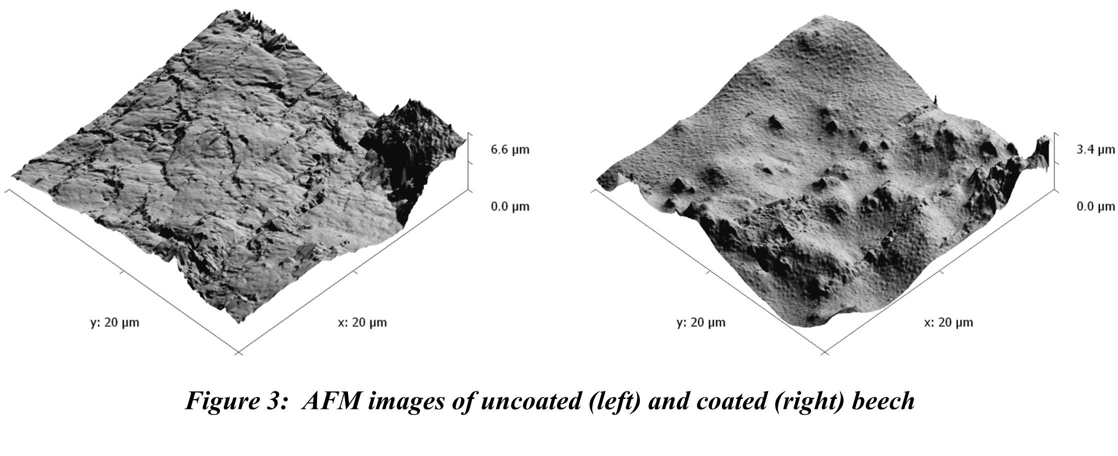

Figure 3: AFM images of uncoated (left) and coated (right) beech

To reduce the impact of the substrate structure on the topographic characteristics of the plasma-generated layer, layers were deposited on microscope slides. AFM images of a coated slide are shown in Figure 4. The nodule-like structure observed on coated beech was also found on coated glass surfaces. Furthermore, a wavy structure was evident on the smooth glass surface that was not observable on the rough wood surface. The right-hand image in Figure 4 shows the nodule-like structure in more detail. By measuring the layer thickness and weight, the layer density ρ and deposition rate D could be estimated. The calculated density is ρ=3 g/cm^3, and the deposition rate of D=0.5 µm/s is much greater than deposition rates under vacuum conditions, which are typically in the region of nanometres per second (Hegemann *et al.* 1999).

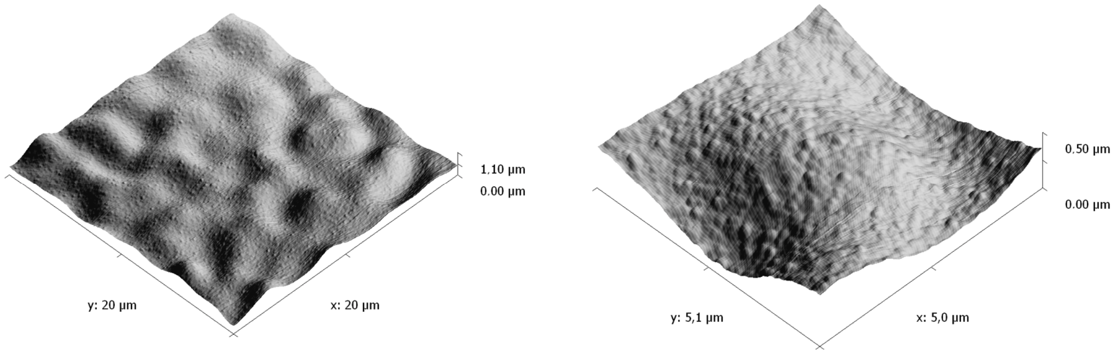

Figure 4: AFM images of coated glass at different magnifications

To determine the elemental and chemical composition of the plasma-generated layer, CHN analysis and FT-IR spectroscopy were performed. To avoid interference by the wood material, the layer for investigation was deposited on microscope slides. CHN analysis revealed the following elemental composition (wt.%): silicon 38%, oxygen 31%, carbon 25% and hydrogen 6%. Despite high amounts of nitrogen in the process gas, no nitrogen was detected within layer material, as also reported by Odrásková *et al.* (2007). The FT-IR results are in accordance with the elemental CHN analysis (Figure 5).

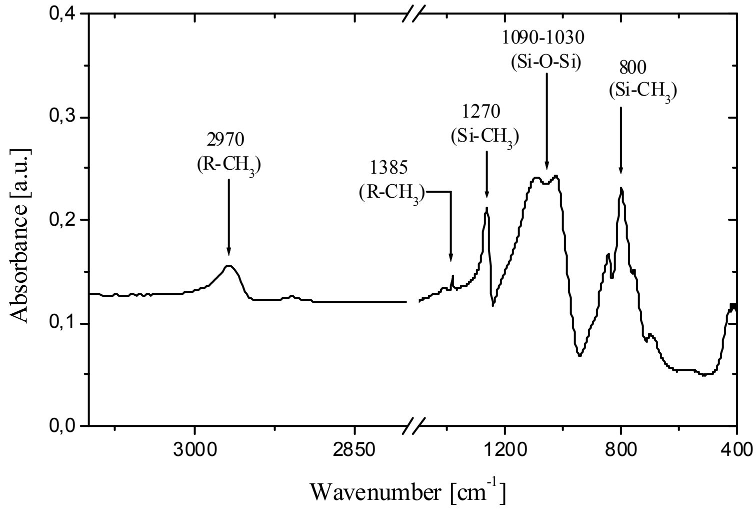

Figure 5 FT-IR spectrum of the plasma-deposited layer

The band at 2970 cm^{-1} is assigned to C–H stretching vibration and that at 1385 cm^{-1} to C–H deformation vibration of R–CH_3 groups. The strong absorption band at 1090–1030 cm^{-1} is attributed to Si–O–Si groups. Si–CH_3 groups can be identified at 1270 and 800 cm^{-1}. According to Denes *et al.* (1999) the relatively high intensity of the band at 850–800 cm^{-1} indicates the presence of a cross-linked structure. These results are in agreement with findings reported by Odrásková *et al.* (2007) and Chen *et al.* (2006), who also investigated HMDSO-based layers generated at atmospheric pressure.

CONCLUSIONS

An atmospheric-pressure plasma jet was used to deposit water-repellent layers on wooden substrates. The dissipated power and the HMDSO concentration affected the water permeability of the deposited layers. An increase in the power level led to a decrease in water permeability, whereas an air/HMDSO–argon ratio of 10:1 yielded the best water impermeability. AFM imaging revealed a compact layer completely covering the substrate surface. The chemical composition determined by CHN analysis and FT-IR spectrometry revealed that carbon, oxygen, silicon and hydrogen are present as R–CH_3, Si–CH_3 and Si–O–Si groups. The deposition of plasma-generated layers is a comprehensive topic and layer performance is determined by many parameters such as the power level, gas mixture, temperature, and experimental configuration. Further research is needed to investigate the influence of these parameters and their effects on layer characteristics such as the surface energy, mechanical properties and long-term stability. Control of these parameters might open up new applications, since layers serving as bonding agents or with biocidal properties could be generated.

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REFERENCES

Bente, M., Avramidis, G., Förster, S., Rohwer, E.G. and Viöl, W. (2004). Wood surface modification in dielectric barrier discharges at atmospheric pressure for creating water repellent characteristics. *Holz als Roh- und Werkstoff*, **62**, 157–163.

Chen, Q., Zhang, Y., Han, E. and Ge, Y. (2006). SiO2-like film deposition by dielectric barrier discharge plasma gun at ambient temperature under an atmospheric pressure. *Journal of Vacuum Science and Technology*, **24**, 2082–2086.

Creatore, M., Palumbo, F. and d'Agostino, R. (2002). Diagnostics and insights on PECVD for gas-barrier coatings. *Pure and Applied Chemistry*, **74**, 407–411.

Custódio, J., Broughton, J., Cruz, H. and Winfield, P. (2009). Activation of timber surfaces by flame and corona treatments to improve adhesion. *International Journal of Adhesion and Adhesives*, **29**, 167–172.

Denes, A., Tshabalala, M., Rowell, R., Denes, F. and Young, R. (1999). Hexamethyldisiloxane-plasma coating of wood surfaces for creating water repellent characteristics. *Holzforschung*, **53**, 318–326.

Evans, P.D., Ramos, M. and Senden, T. (2007). Modification of wood using a glow discharge plasma derived from water. In: *Proceedings of the Third European Conference on Wood Modification*, Bangor, Wales, pp. 123–132.

Hegemann, D., Vohrer, U., Oehr, C. and Riedel, R. (1999). Deposition of SiO_x films from O_2/HMDSO plasmas. *Surface and Coatings Technology*, **116–119,** 1033–1036.

Hippler, R., Pfau, S., Schmidt, M. and Schoenbach, K.H. (Eds.) (2001). *Low Temperature Plasma Physics*. Wiley-VCH Verlag, Berlin, Germany.

Inagaki, N. (1996). *Plasma Surface Modification and Plasma Polymerization*. CRS Press, Boca Raton, FL, USA.

Janzen, G. (1992). *Plasmatechnik, Grundlagen/Anwendung/Diagnostik.* Hüthig, Heidelberg, Germany.

Klarhöfer, L., Maus-Friedrichs, W., Kempter, V. and Viöl, W. (2005). Investigation of pure and plasma-treated spruce with surface analytical techniques. In: *Proceedings of the Second European Conference on Wood Modification*, Göttingen, Germany, pp. 339–345.

Kogelschatz, U. (2003). Dielectric-barrier discharges: Their history, discharge physics and industrial applications. *Plasma Chemistry and Plasma Processing*, **23**, 1–46.

Kress, L., Wessely, B. and Ripperger, S. (1999). Das Eindringen von Wassertropfen in unbehandeltes und holzschutzmittelbehandeltes Holz. *Wissenschaftliche Zeitschrift TU Dresden*, **48**, 23–26.

Mahlberg, R., Niemi, H.E.M., Denes, F. and Rowell, R.M. (1998). Effect of oxygen and hexamethyldisiloxane plasma on morphology, wettability and adhesion properties of polypropylene and lignocellulosics. *International Journal of Adhesion and Adhesives*, **18**, 283–297.

Odrásková, M., Szalay, Z., Ráhel, J., Zahoranová, A. and Cernák, M. (2007). Diffuse coplanar surface barrier discharge assisted deposition of water repellent films from N_2/HMDSO mixtures on wood surface. In: *Proceedings of the 28th International Conference on Phenomena in Ionized Gases*, Prague, Czech Republic, pp. 803–806.

Odrásková, M., Stahel, P. and Smolar, M. (2008a). Surface barrier discharge assisted deposition of water repellent films from N_2/HMDSO mixtures on surface of poplar veneer In*: Proceedings of the IEEE Third International Conference on Plasma Science,* Karlsruhe, Germany.

Odrásková, M., Ráhel, J., Zahoranová, A., Tino, R. and Cernák, M. (2008b). Plasma activation of wood surface by diffuse coplanar surface barrier discharge. *Plasma Chemistry and Plasma Processing*, **28**, 203–211.

Podgorski, L., Chevet, B., Onic, L. and Merlin, A. (2000). Modification of wood wettability by plasma and corona treatments. *International Journal of Adhesion and Adhesives*, **20**, 103–111.

PSE 2006 (2007). *Proceedings of the 10th International Conference on Plasma Surface Engineering,* Garmisch-Partenkirchen, Germany.

Rehn, P., Wolkenhauer, A., Bente, M., Förster, S. and Viöl, W. (2003). Wood surface modification in dielectric barrier discharges at atmospheric pressure. *Surface and Coating Technology*, **174–175**, 515–518.

Topala, I. and Dumitrascu, N. (2007). Dynamics of the wetting process on dielectric barrier discharge (DBD)-treated wood surfaces. *Journal of Adhesion Science and Technology*, **21**, 1089–1096.

Vautrin-Ul, C., Roux, F., Boisse-Laporte, C., Pastol, J.L. and Chausse, A. (2002). Hexamethyldisiloxane (HMDSO)-plasma-polymerised coating as primer for iron corrosion protection: Influence of RF bias. *Journal of Material Chemistry*, **12**, 2318–2324.

Wang, J., Wang, Y., Zhou, X., Jin, Z. and Yu, Z. (2003). Deposition and characteristics of atomic oxygen protective coatings using plasma polymerized HMDSO. In: *Protection of Materials and Structures from Space Environment: Icpmse-6*. Kleiman, J., Iskanderova, Z. (Eds.), Springer, Netherlands, pp. 443–450.

Wolkenhauer, A., Avramidis, G., Hauswald, E., Militz, H. and Viöl, W. (2008a). Plasma treatment of wood-plastic composites to enhance their adhesion properties. *Journal of Adhesion Science and Technology*, **22**, 2025–2037.

Wolkenhauer, A., Avramidis, G., Militz, H. and Viöl, W. (2008b). Plasma treatment of heat treated beech wood – Investigation on surface free energy. *Holzforschung*, **62**, 472–474.

Wolkenhauer, A., Militz, H. and Viöl, W. (2008c). Increased PVA-glue adhesion on particle board and fibre board by plasma treatment. *Holz als Roh- und Werkstoff*, **66,** 143–145.

Wolkenhauer, A., Avramidis, G., Hauswald, E., Militz, H. and Viöl, W. (2009). Sanding vs. plasma treatment of aged wood: A comparison with respect to surface energy. *International Journal of Adhesion and Adhesives*, **29**, 18–22.