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Modification of wood by low-temperature atmospheric discharge plasma

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Abstract: *Modification of wood by low-temperature atmospheric discharge plasma.* Discharge plasma at atmospheric pressure was used to improve the wetting and adhesion properties of wood. Although also low-pressure plasma processes and namely atmospheric pressure processes are more attractive for wood industry applications because of their lower cost, higher throughput, and ability to operate in-line without vacuum systems. Atmospheric pressure plasma system is typically based on volume diffuse barrier discharge arrangement, where the treated material is placed between the discharge electrodes. However, using the sessile droplet technique, we have identified a significant increase of polar component of surface free energy. Polar part of surface free energy is associated with the presence of acid/base forces (electron donor–acceptor bonds). The treatment of wood exhibited a substantial aging effect; nevertheless the treated surface never recovers to its initial hydrophobic state. The enhancement of wood wettability is a necessary condition to promote a better adhesion with a water-based adhesives and coatings, which is currently being studied. The involvement of planar plasma source in our case makes the quality of the plasma treatment completely independent on the thickness and electrical conductivity of the wood material treated.

INTRODUCTION

The concept of wood bonding after electric discharge plasma surface modification is of considerable interest with the respect to construction of the strongest wood adhesive joints (1 -3). Great efforts have been made in developing various kinds of furniture using plastic or wood veneers in adhesive joints wood-adhesive-veneer.

Among numerous kinds of electric discharge plasmas, coplanar surface barrier plasma at atmospheric pressure and/or radio-frequency volume plasma at reduced pressure are currently the most promising methods of surface modification, and are considered as the ‘green’ ecologically friendly modification method (4). For a common industrial wood application various woods have to possess a large set of various surface characteristics, including polarity (hydrophobicity or hydrophilicity), dyability, scratch resistance, tailored adhesive properties, antibacterial resistance etc. Nanoscale changes to the surface of wood materials enable the changes in materials surface, while maintaining the desirable bulk material properties.

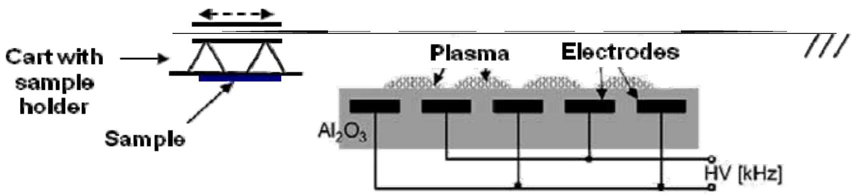
EXPERIMENTAL

Materials

Wood boards, wood particles (oak) (TU Zvolen, Slovakia), ChS Epoxy 510 (Czech Republic), testing liquids (water, ethylene glycol, formamide, diiodmethane, 1-bromnaphthalene, dischlormetane.

Modification method

In this contribution the modified wood filler/particles (d < 50 micrometer) were investigated using diffuse coplanar barrier surface discharge (DCSBD) plasma of selected wood kind (oak wood particles), for potential applicability in woodworking industry. The selected wood was modified by DCSBD plasma. There are two reasons why in the case of wood to apply plasma discharge modification. Firstly, plasma in air itself significantly increases hydrophilicity of the wood surface, 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 material. Second reason for the plasma use is to increase adhesion in adhesive joint between wood particles in fiberboard material, or wood-wood and/or wood-polymer (e.g. polyvinylchloride, other plastic foils) for industrial applications due to growth of wood wettability.



Scheme 1. Source of DCSBD plasma for wood modification

Plasma modification was implemented in static conditions by DCSBD plasma technology (Fig. 1) of laboratory scale with oxygen as the gaseous medium at atmospheric pressure and room temperature. A schematic profile of the plasma system is given in Scheme 1. It basically comprises a series of parallel metallic electrodes inset inside a ceramic dielectric located in a glass chamber, which allows the carrier gases to flow. All samples were treated on both sides with plasma power of 300 W. The improvement of hydrophilicity and/or hydrophobicity of the wood, its surface properties, the improvement of strength of adhesive joint of wood/wood composites with epoxy resin were studied for the determination of the appropriate structure of the plasma modified wood surfaces.

Contact angles, surface energy measurement

The surface energy of oak wood was determined using contact angles measurements with selected testing liquids set using SEE (Surface Energy Evaluation) device completed with a web camera (Advex, Czech Republic) and necessary PC software.
The drop of the testing liquid (V = 20 μl) was placed with a micropipette (Biohit, Finland) on the polymer surface, and a contact angle of the testing liquid was measured. The contact angle of wood surface was measured instantly after placing of the liquid drop.
The surface energies of wood were evaluated by Owens-Wendt-Rabel-Kaelble (OWRK) equation modified by the least squares method [1]:

$$\frac{(1+\cos\theta)\gamma_{LV}}{2} = \left(\gamma_{LV}^{d}\gamma_{s}^{d}\right)^{1/2} + \left(\gamma_{LV}^{p}\ \gamma_{s}^{p}\right)^{1/2} \qquad (1)$$

where

θ = contact angle of testing liquid (deg),

γ_{LV} = surface energy of the testing liquid ($mJ.m^{-2}$),

$\gamma_{LV}^{d}, \gamma_{LV}^{p}$ = dispersive component (DC), and polar component (PC) of surface energy of the testing liquid ($mJ.m^{-2}$),

$\gamma_{s}^{d}, \gamma_{s}^{p}$ = DC, and PC of surface energy of the wood ($mJ.m^{-2}$).

RESULTS AND DISCUSSION

Figure 1 shows the contact angle of re-distilled water deposited on oak wood surface modified by DCSBD plasma in oxygen vs. time of activation. The contact angle of water was measured immediately after deposition of the water drop. The contact angles of water decreased with time of the activation. The contact angles of water showed a steep decrease from 78^{o} to 45^{o} after short time of activation by DCSBD plasma (5 s). The changes of the contact angle were substantially lower for longer time of modification by plasma and this plot was levelled off. The decrease of the contact angles of polar testing liquids can be explained by an increase of the hydrophilicity of oak wood surface due to the treatment by DCSBD plasma in oxygen. The hydrophilicity of the surface depends on the formation of polar oxygenic functional groups on wood surface during the modification by oxygen plasma. After saturation of the polymer surface with polar groups the hydrophilicity as well as the values of contact angle of testing liquids were stabilized.

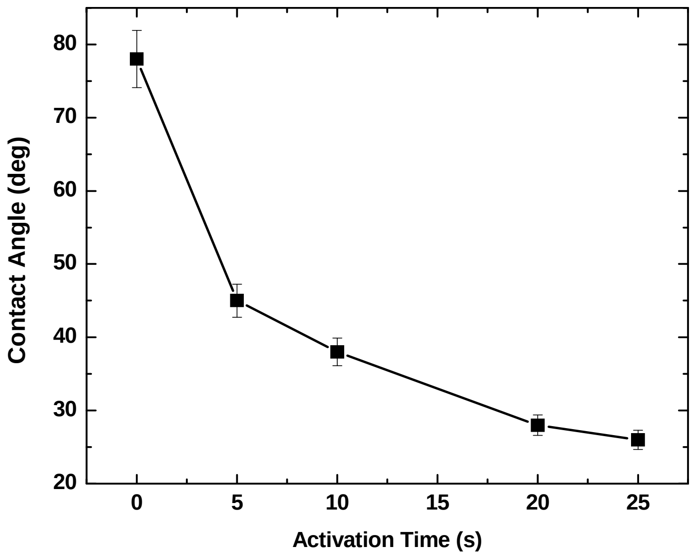


Figure 1. Contact angle of water deposited on oak wood surface modified by DCSBD plasma on oxygen vs. activation time

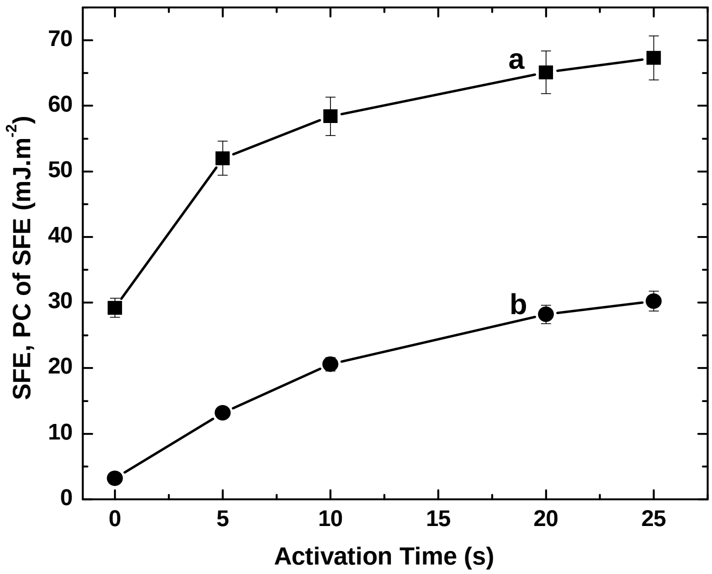


Figure 2. Surface energy (plot a) and its polar component (b) of oak wood modified by DCSBD plasma in oxygen vs. activation time

The surface properties of oak wood modified by DCSBD plasma in oxygen are illustrated in Figure 2. The surface energy and its polar component of wood increased with time of activation. The surface energy of oak wood treated 5 s by DCSBD plasma in oxygen increased from 29 $mJ.m^{-2}$ (pristine sample) to 52 $mJ.m^{-2}$, and the polar component of the surface energy increased from 3.2 $mJ.m^{-2}$ to 13.2 $mJ.m^{-2}$. If the longer activation time was applied the plots in Figure 2 levelled off. This fact relates to saturation of wood surface with oxygen-containing functional groups due to modification by DCSBD plasma, and the changes in surface energy were very small when modification by plasma for more than 5 s was applied.

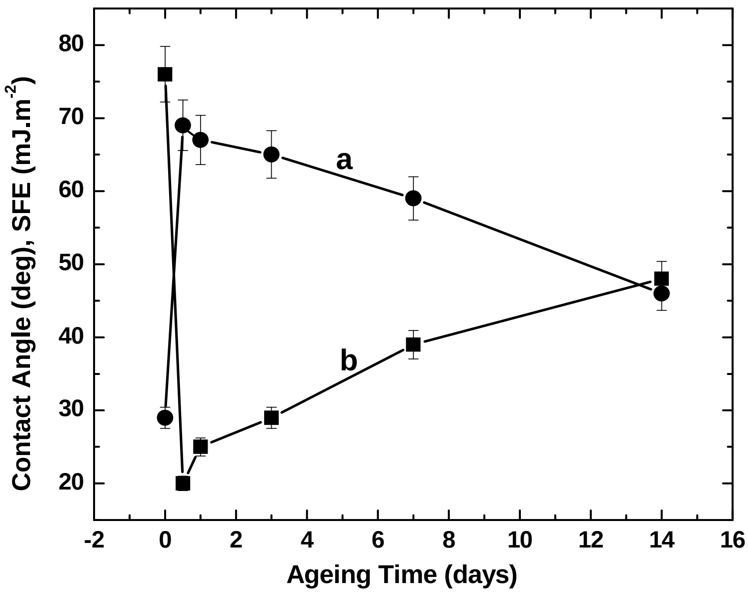


Figure 3. Surface energy (plot a) and contact angle (plot b) of oak wood surface modified by DCSBD plasma in oxygen vs. ageing time

Figure 3 represents the dependence of surface energy (plot a) and contact angle (plot b) of water of oak wood pre-treated by DSBD plasma in oxygen during ageing. According to Figure 3 the surface energy of wood decreased significantly from 68 to 46 mJ.m^{-2} after 5 s of modification by DCSBD plasma. The contact angle of oak wood modified by plasma during ageing increased from 20^{o} up to 48^{o}. These changes relate to hydrophobic recovery of wood surface modified by plasma during ageing.

Figure 4 shows the shear strength of adhesive joint oak wood modified by DCSBD plasma in oxygen –epoxy adhesive vs. activation time. The shear strength of adhesive joint wood modified by plasma – epoxy increases non-linearly with activation time from 1.6 MPa (pristine oak wood) up to 4.6 MPa (25 s activation by plasma).

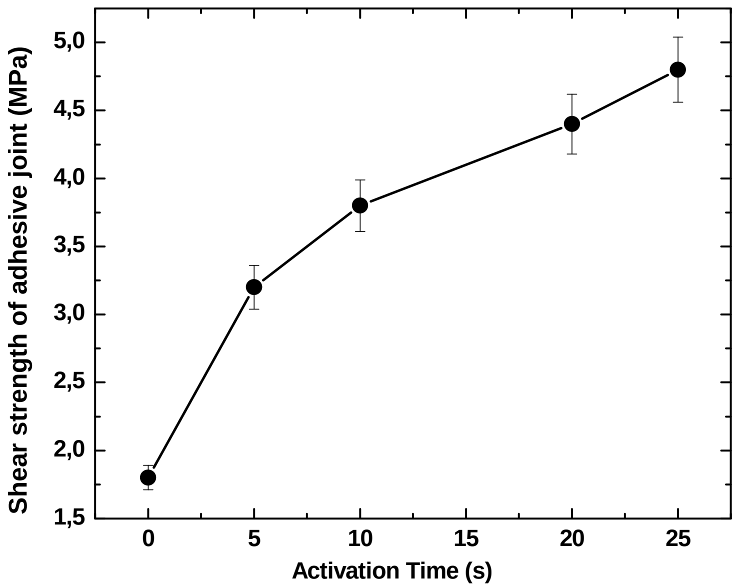


Figure 4. Shear strength of adhesive joint oak wood modified by DCSBD plasma in oxygen vs. activation time

CONCLUSION

The contact angles of water showed a steep decrease from 78° to 45° after short time of activation by DCSBD plasma in oxygen (5 s). The changes of the contact angle were substantially lower for longer time of modification by plasma and this plot was levelled off. The surface energy and its polar component of wood increased with time of activation. The surface energy of oak wood treated 5 s by DCSBD plasma in oxygen increased from 29 $mJ.m^{-2}$ (pristine sample) to 52 $mJ.m^{-2}$, and the polar component of the surface energy increased from 3.2 $mJ.m^{-2}$ to 13.2 $mJ.m^{-2}$. Surface energy of wood decreases significantly from 68 $mJ.m^{-2}$ to 46 $mJ.m^{-2}$ after 5 s of modification by DCSBD plasma. The contact angle of oak wood modified by plasma during ageing increased from 20^o up to 48^o. These changes relate to hydrophobic recovery of wood surface modified by plasma during ageing. The shear strength of adhesive joint wood modified by DCSBD plasma in oxygen-epoxy increases significantly with activation time from 1.6 up to 4.6 MPa.

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REFERENCES

1. Biederman, H., Osada, Y. Plasma polymerisation processes. Elsevier, Amsterdam,1992.
2. Denes, R., Tshabalala, A., Rowell, R., Denes, F., Young, A. Hexamethyldisiloxane-plasma coating of wood surfaces for creating water repellent characteristics. Holzforschung 53 (1999), pp. 318-326.
3. Kamdem, D. P., Pizzi A., Triboulot M. C. Heat-treated timber: potentially toxic byproducts presence and extent of wood cell wall degradation. Holz Roh- Werkstoff 58 (2000), pp. 253–257.
4. Kiguchi, M. Surface modification and activation of wood. In: Hon D. N. (ed.), Chemical modification of lignocellulosic materials. Marcel Dekker, New York, 1996, pp 197-227.

Streszczenie. *Modyfikacja drewna niskotemperaturowym wyładowaniem plazmowym.* Wyładowanie plazmowe zostało wykorzystane dla polepszenia zwilżalności i adhezji drewna. Niskociśnieniowe oraz atmosferyczne technologie plazmowe są bardziej atrakcyjne dla przemysłu ze względu na niższe koszty, wyższą wydajność i brak konieczności posiadania systemów próżniowych. Modyfikacja drewna spowodowała efekt starzenia, jednakże powierzchnia nie wraca do wyjściowych parametrów hydrofobowych. Polepszenie zwilżalności powoduje zwiększenie adhezji wodnych klejów i materiałów lakierniczych. Zastosowanie płaskiego źródła plazmy spowodowało że jakośćobróki jest niezależna od grubości oraz przewodności elektrycznej drewna.