Annals of Warsaw University of Life Sciences - SGGW
Forestry and Wood Technology No 90, 2015: 131-134
(Ann. WULS - SGGW, For. and Wood Technol., 90, 2015)

Oak wood modification using cold plasma

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Abstract: *Oak wood modification using cold plasma*. The contact angles of water on oak wood surface showed a steep decrease after activation by cold plasma in air. The surface energy and its polar component of oak wood increased with time of activation by plasma. The surface energy of oak wood treated by radio-frequency (RF) plasma in air increased from 62 $mJ.m^{-2}$ (pristine wood) to 74 $mJ.m^{-2}$ (plasma-modified wood), and the polar component of the surface energy increased from 17.0 $mJ.m^{-2}$ to 27.8 $mJ.m^{-2}$. The shear strength of adhesive joint of oak wood with epoxy adhesive increases non-linearly with activation time from 5.6 MPa to 8.8 MPa.

Keywords: epoxy adhesive, oak wood, surface properties, radio-frequency plasma, modification, formaldehyde, adhesive bonding.

INTRODUCTION

The bonding of wood modified by low-temperature plasma is of considerable interest with the respect to construction of the strongest wood adhesive joints (***Kiguchi 1996***, ***Kamdem et al. 2000, Wolkenhauer et al.2009***). Great efforts have been made in developing various kinds of furniture using wood or plastics veneers in adhesive joints wood-adhesive-veneer. The low-temperature discharge plasma has been used to improve the wetting and adhesion properties of wood. The pre-treatment of wood surface using discharge plasma is attractive for various wood applications mainly because of their lower cost. However, we have identified a significant increase of polar component of wood surface energy after modification by low-temperature plasma. Polar component of surface energy is associated with the presence of acid-base forces (electron donor-acceptor bonds). The treatment of wood exhibited a substantial aging effect, but the modified surface never recovers to its initial hydrophobic state. The enhancement of wood hydrophilicity is a necessary condition to promote a better adhesion with a water-based adhesives and coatings, which is currently being studied. The radio-frequency (RF) discharge plasma at reduced pressure is currently an efficient method for treatment of surface and adhesive properties of wood, and is considered as the “green” ecologically friendly method (***Denes et al. 1999, Acda et al. 2012, Moghadamzadeh et al. 2011***).For a common industrial wood application various woods have to possess a large set of various surface characteristics, including polarity, dyeability, scratch resistance, tailored adhesive properties, antibacterial resistance etc. The nanoscale dimension changes of the plasma-treated wood have been carried out, while maintaining the desirable bulk material properties.

EXPERIMENTAL

Materials

Oak wood plates with dimensions 50×15×5 mm (Technical University in Zvolen, Slovakia), ChS Epoxy 510, Telalit T 410 (Spolchemie, Czech Republic), 5 testing liquids set (re-distilled water, ethylene glycol, formamide, diiodmethane, α-bromonaphthalene), dichlorometane (Merck, Germany).

Modification method

In this paper, the oak wood surface was pre-treated by RF-discharge plasma. There are three reasons why in the case of wood to apply low-temperature plasma modification. Firstly, discharge plasma in air itself significantly increases hydrophilicity of the wood, 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 an increase of adhesion in adhesive joint between wood substrate, which is important for industrial applications due to growth of wood wettability. Third reason is a creation of stronger bonds to bind formaldehyde molecules usually releasing from polycondensation adhesives.

The modification of wood by the capacitively coupled RF-plasma was performed in a laboratory RF-plasma reactor (Scheme 1) working at reduced pressure 80 Pa consists of two 240-mm brass parallel circular electrodes with symmetrical arrangement, 10 mm thick, between which RF-plasma was created.

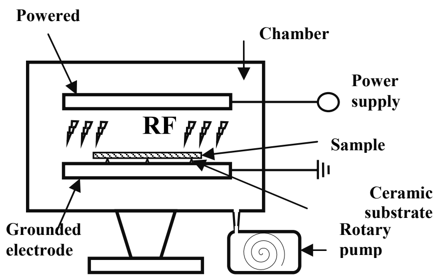

Fig. 1 RF-plasma source

The electrodes of RF-plasma reactor are placed in a locked-up stainless steel vacuum cylinder. The one is powered and the other one is grounded together with steel cylinder. The voltage of RF-plasma reactor is 2 kV, frequency 13.56 MHz, current intensity was 0.6 mA, and the max. power of the RF-plasma source is 1200 W. The wood samples were modified by RF-plasma at the power 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 adhesive were studied for the determination of the appropriate structure of the plasma modified wood surfaces. 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 testing liquid drop on the wood surface was measured instantly after placing. The surface energies of wood were evaluated by Owens-Wendt-Rabel-Kaelble (OWRK) equation (***Novák et al. 2012***).

RESULTS AND DISCUSSION

The contact angle of water drop on the beech wood surface was measured immediately after drop deposition. The contact angles of water decreased with time of the activation by RF-plasma. The contact angles of water showed a steep decrease from 68^o (pristine sample) to 44^o after 120 s activation of wood by RF-plasma in air. The decrease of the contact angles of polar testing liquid (water) can be explained by an increase of the hydrophilicity of beech wood surface due to the treatment by RF-plasma in air. The hydrophilicity of the surface depends on the formation of polar oxygenic functional groups on wood surface during the plasma modification in air. After saturation of the polymer surface with polar groups the hydrophilicity was stabilized.

The surface energy and its polar component of oak wood increased with time of RF-plasma activation. The surface energy of wood treated 120 s by RF-plasma in air increased from 62 mJ.m^{-2} (pristine sample) to 74 mJ.m^{-2}, and the polar component of the surface energy increased from 17.0 mJ.m^{-2} (pristine sample) to 27.8 mJ.m^{-2} (120 s). If the longer activation time was applied the changes of surface energy and its polar component were very small. This fact relates to saturation of wood surface with oxygen-containing functional groups due to modification by RF-plasma.

CONCLUSIONS

The contact angles of water deposited on oak wood surface showed a steep decrease after activation by RF plasma in air. The surface energy and its polar component of oak wood increased with time of activation by plasma. The surface energy of oak wood treated by RF-plasma in air increased from 62 mJ.m^{-2} (pristine sample) to 74 mJ.m^{-2}, and the polar component of the surface energy increased from 17.0 mJ.m^{-2} to 27.8 mJ.m^{-2}. The shear strength of adhesive joint of oak wood with epoxy adhesive increased non-linearly with time of modification by plasma from 5.6 MPa to 8.8 MPa.

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Streszczenie: *Modyfikacja drewna dębowego przy użyciu zimnej plazmy*. Kąty zwilżania kropli wody na powierzchni drewna dębowego po aktywacji zimną plazmą charakteryzowały się stromym spadkiem. Energia powierzchniowa i jego polarny składnik na powierzchni drewna dębowego wzrastała z czasem aktywacji tej powierzchni plazmą. Energia powierzchniowa wzrosła z 62 mJ□m^{-2} (drewno niemodyfikowane) do 74 mJ□m^{-2} (drewno modyfikowane plazmą), a składnik polarny tej energii wzrósł z 17,0 mJ.m^{-2} do 27,8 mJ□m^{-2}.

Zaobserwowano również nieliniowy wzrost wytrzymałości na ścinanie klejonego drewna dębowego (klejem epoksydowym) z czasem aktywacji plazmą (z 5,6 MPa do 8,8 MPa).

Acknowledgements: *This contribution was supported by Ministry of Education of Slovak Republic, and Slovak Academy of Sciences, project VEGA, No. 2/0199/14.*

This research was supported by a Slovakian Agency SRDA; project APVV-14-0506 "ENPROMO".

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