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Investigation of beech wood modified by radio-frequency discharge plasma

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ABSTRACT

Low-temperature plasma was used to improve the surface and adhesive properties of wood. The pre-treatment of wood surfaces using radio-frequency (RF) discharge plasma is attractive for various wood applications, mainly because of the high efficiency and low production cost of the process. In addition, a significant increase in the polar component of the wood surface energy, which is associated with the presence of acid–base interactions (electron donor–acceptor bonds), after modification by RF discharge plasma was identified. The treatment of wood by RF plasma exhibited an aging effect, with the modified surface never recovering its initial hydrophobic state. Indeed, the enhancement of the wettability of wood is necessary for promoting better adhesion with water-based adhesives and coatings, which is currently the subject of ongoing study.

1. Introduction

The bonding of wood after discharge plasma surface modification is of considerable interest for constructing the strongest wood adhesive joints possible [1]. The low-temperature plasma used to treated wood surfaces leads to improvements in the bonding of wood to various substrates via adhesives. There are two reasons why discharge plasma is applied for the surface treatment of wood. First, discharge plasma in air alone significantly increases the hydrophilicity of wood due to the formation of various polar groups (e.g., hydroxyl, carbonyl, and carboxyl groups), and the macromolecules in wood serve as cross-links (measuring up to a few microns long), which leads to an increase in scratch resistance and to an improvement in the barrier properties of the wood material [2]. Second, the application of discharge plasma enhances the bonding of joints between polymeric adhesives and wood substrates due to the increase in the wettability of wood, which is important for industrial applications. A low-temperature plasma is a mixture of various excited particles, such as ions, atoms, electrons, and radicals, with low degrees of ionization and low penetrating energy; however, the particles in such as plasma have sufficient energy to break chemical bonds in wood substrates [3]. The effects of the discharge plasma treatment of wood are limited to a few nanometers beneath the substrate surface and thus do not affect the bulk properties of wood [4]. The increase in surface polarity due to oxidation reactions induced during the modification of wood by RF plasma improves the wettability and hydrophilicity of wood [5]. This improved wettability assists in establishing molecular-scale contact with the wood surface and it is critical to the development of strong adhesion at the adhesive/wood interface. Great efforts have been made in developing various types of furniture using wood or plastic veneers in adhesive wood-adhesive-veneer joints [6]. The application of cold plasma is currently an effective method for the modification of the surface and adhesive properties of wood and is considered a “green”, environmentally friendly method [7–12]. For common industrial wood applications, various woods must possess a large set of surface characteristics, including polarity (hydrophobicity or hydrophilicity), dyeability, scratch resistance, tailored adhesive properties, and antibacterial resistance. Nanoscale changes in the surface of wood materials allow the materials to exhibit novel surface properties while maintaining their desirable bulk properties [13–17]. Some short preliminary experiments have been carried out [18].

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This study focuses on the more detailed investigation of the surface and adhesive properties, chemical composition, and physical changes of beech wood modified by RF discharge plasma. The aging effect exerted by the plasma treatment on the beech wood was also investigated.

2. Experimental

2.1. Materials

Beech wood plates with semi-radial faces and 8% moisture content were planed on tested side and then cut to dimensions of 50 × 15 × 5 mm and the surface was treated using very fine sandpaper (Technical University in Zvolen, Slovakia), the water-based polyurethane adhesive Dispercoll U 53 (Bayer, Germany), a set of 5 testing liquids (re-distilled water, ethylene glycol, formamide, diiodomethane, 1-bromonaphthalene (Merck, Germany)) for contact angle measurements, and dichloromethane (Fluka, Germany) for the degreasing of surfaces were used in this study.

2.2. Modification method

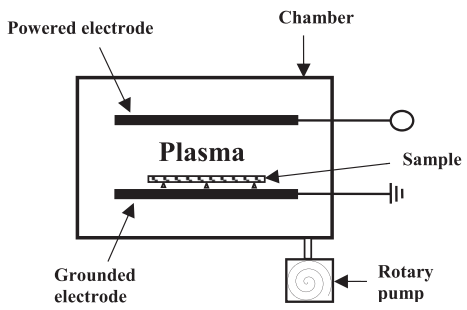
The surface of the beech wood samples were treated in air as processing gas by capacitively coupled radio-frequency (CCRF) discharge plasma in a laboratory-scale CCRF plasma system (Scheme 1) operated at a reduced pressure of 80 Pa. The system consists of two circular brass electrodes with dimensions 240 mm in diameter and 10 mm in thickness placed parallel to one another, between which a CCRF plasma was created.

The electrodes of the CCRF plasma system were placed in a sealed stainless steel vacuum cylinder, with one of the electrodes powered and the other one grounded to the steel cylinder. The voltage of the CCRF plasma reactor is 2 kV, the frequency 13.56 MHz, the maximum current intensity 0.6 mA, and the maximum power of the CCRF plasma source 1200 W. The wood samples were modified by CCRF plasma at the source power of 300 W.

The improvement in the hydrophilicity of the wood samples, the surface properties, and the improvement in the strength of the joints formed between wood/wood composites with water-based polyurethane adhesive were studied to determine the appropriate structure of the plasma-modified wood surfaces.

2.3. Measurements methods

The surface free energy (SFE) of beech wood was determined by the contact angles measurement of a set of 5 test liquids with different polarity and 8 replicated measurements were used to test contact angle for each testing liquid. Drops of the test liquids (V = 5 μl) were placed on the surface of the wood samples with a micropipette (Biohit, Finland), and the dependence θ = f (t) was extrapolated to t = 0. The SFE of the beech wood samples was determined by contact angle measurements using a professional SEE (Surface Energy Evaluation) device equipped with a web camera (Advex, Czech Republic) and the appropriate PC software. The SFE of the wood as well as the corresponding polar and dispersive components of the SFE (PC SFE and DC SFE, respectively) were evaluated by the Owens–Wendt–Rabel–Kaelble (OWRK) method modified by incorporating at least squares method [5].



Scheme 1. Scheme of CCRF plasma system.

The surface morphology of the plasma-treated beech wood samples was measured by atomic force microscopy (AFM). All measurements were performed under ambient conditions using a commercial atomic force microscope (NanoScope Dimension IIIa, MultiMode Digital Instruments, USA) equipped with a PPP-NCLR tapping-mode probe (Nanosensors, Switzerland; spring constant: 39 N m^{-1}, resonant frequency ~ 180 kHz).

Nanoindendentation analysis was performed using a Hysitron TriboLab Nanomechanical Test Instrument (equipped with a scanning probe microscope; SPM) and a Berkovich probe. The TI 750 Ubi nanomechanical test instrument is a dedicated scanning nanoindenter. The system is equipped with Hysitron's in situ SPM imaging capability and a performance control unit. The nanometer-resolution in situ imaging, tip-positioning ability, increased sensitivity, and feedback rate of the TI 750 Ubi and performance control unit allows for low displacement and high-resolution testing.

The morphology of the wood samples before and after CCRF plasma irradiation was investigated by scanning electron microscopy (SEM) (JSM-6400, JEOL, Japan). Prior to imaging, the surfaces of the test samples were sputter-coated (SCD 050, BALTEC) with a Pt layer (4 nm).

Fourier transform infrared spectroscopy-attenuated total reflectance (ATR-FTIR) measurements were performed with an FTIR ™NICOLET spectrometer (Thermo Scientific, USA) 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.

X-ray photoelectron spectroscopy (XPS) data were recorded using a Thermo Scientific K-Alpha XPS system (Thermo Fisher Scientific, UK) equipped with a micro-focused, monochromatic Al Kα X-ray source (1486.6 eV). An X-ray beam with a spot size of 400 μm size was used at 6 mA × 12 kV. Spectra were acquired in the constant analyzer energy mode with a pass energy of 200 eV for the survey. Narrow regions were collected using the snapshot acquisition mode (150 eV pass energy), enabling rapid collection of data (5 s per region). Charge compensation was achieved with the system's flood gun, which provides low-energy electrons (0 eV) and low-energy argon ions (20 eV) from a single source. The argon partial pressure was 2 × 10^{-5} Pa in the analysis chamber. The Thermo Scientific Advantage software, version 4.88 (Thermo Fisher Scientific), was used for digital acquisition and data processing. Spectral calibration was performed using the automated calibration routine and the internal standards of Au, Ag and Cu that were supplied with the K-Alpha system.

The surface compositions (in atomic %) of the samples were determined by considering the integrated peak areas of the detected atoms and the respective sensitivity factors. The fractional concentration of a particular element A was computed as follows:

$$\%A = \frac{I_A/s_A}{\sum(I_n/s_n)} \times 100\%, \quad (1)$$

where I_n and s_n are the integrated peak areas and the Scofield sensitivity factors corrected for the analyzer transmission, respectively.