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Surface free radicals detection using molecular scavenging method on black spruce wood treated with cold, atmospheric-pressure plasmas

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ABSTRACT

Formation of surface free radicals on wood surfaces during plasma treatment could be an important factor when it comes to wood coating adhesion enhancement. In order to explore this aspect, freshly sanded black spruce (*Picea mariana*) wood samples were exposed to either plane-to-plane atmospheric-pressure dielectric barrier discharge (AP-DBD) or the flowing afterglow of an AP-DBD and then dipped in a 2,2-diphenyl-1-picrylhydrazyl (DPPH) solution. Wood veneers (extracted to eliminate small molecules prior to each plasma treatment) showed an increase of their reaction rate toward DPPH after treatment in the AP-DBD operated in nominally pure He; a feature ascribed to the plasma-assisted formation of free radicals on the wood surface. Addition of trace amounts (0.1%) of O_2 in the He plasma produced a decrease in DPPH reactivity, suggesting that oxygen–spruce interaction during plasma treatment quenches free radicals formation. Similar experiments performed using the flowing afterglow of AP-DBD operated in either N_2 or N_2/O_2 showed that both treatments do not generate significant amount of surface free radicals. This partially results from oxygen–wood interactions due to the open-air configuration of the afterglow reactor.

1. Introduction

Plasmas are now widely used to enhance adhesive bond strength on wood surfaces [1–3]. This technology comes in a variety of forms and types. The most prevalent are low-pressure plasmas (sustained by direct-current, radio frequency, or microwave electromagnetic fields), corona discharges, and cold, atmospheric-pressure plasmas such as dielectric barrier discharges (DBDs). All of these plasmas have their own advantages, but the latter is notably interesting for wood surface modification in regard to the wood industry since atmospheric-pressure plasmas can easily be implemented in a production line, requiring no controlled pressure unit and generating only a small-to-inexistent amount of chemical waste [4]. In addition, the neutral gas temperature in such systems is close to 300 K, making it suitable for the treatment of heat-sensitive polymers such as wood. Generally, these plasmas are composed of charged and neutral species (molecules or atoms), electrons, and photons ranging from ultraviolet to infrared [5] and all of these species can induce changes on wood surfaces [6]. For example, Klarhöfer et al. [7] showed that the O/C ratio could be increased following air plasma exposure of a wood surface. Although research conducted on wood samples exposed to such plasmas have revealed that plasma-induced modification can increase wood-coating adhesion [8–11], the physics and chemistry driving these enhancements remain poorly understood. In most studies, the formation of more hydrophilic wood surfaces is targeted to increase polar interaction with the coatings [6,12]. However, in some cases, plasma-induced hydrophobization of wood surfaces can also improve coatings adhesion as reported by Busnel et al. [13].

In addition to wettability changes, the presence of positive ions, electrons, metastable species, reactive atoms and molecules, and photons in plasmas could also generate surface free radicals that are likely to play a critical role in the evolution of the wood-coating adhesion properties. Those unpaired electrons are highly interesting for wood adhesion properties as they could quickly react with coatings to form permanent chemical bonds. According to previous studies, both low- and atmospheric-pressure plasmas can generate surface free radicals on natural and synthetic polymers [14–16]. Indeed, common neoprene-based contact adhesives do work by

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such a free-radical mechanism. Wood is thus not excluded for surface free radial formation following plasma treatment since it is formed by an assembly of different natural polymers.

The presence of surface free radicals can be measured using either electron spin resonance (ESR) spectroscopy, nitric oxide gas coupled with X-ray Photoelectron Spectroscopy (XPS) measurements, or a chemical scavenger. Even if the ESR technique is known to provide an absolute detection measurement, it requires instrument access near the plasma source to ensure minimal time between plasma treatment and ESR analysis [17]. In the case of nitric oxide, the samples need to be directly transferred in a second chamber after plasma treatment in order to avoid reaction with oxygen and nitric oxide contamination [18,19]. A simpler and more traceable method relies on the use of a chemical scavenger that can be diluted in a solvent in which the sample can be immersed in order to react with the proper molecules. By measuring the concentration of these molecules with a spectrophotometer and then comparing the untreated and treated surfaces, it is possible to observe the variation in reactivity toward antioxidant functional groups such as carbonyl, carboxyl, hydroxyl and free radicals species. According to Poncin-Epaillard et al. [20], 2,2-diphenyl-1-pricylhydrazyl (DPPH) contains a stable free radical, which is a good candidate for such experiments. This molecule was already successfully used to evaluate the scavenging or antioxidant properties of wood compounds such as lignin and extractives [21]. According to Brand-Williams [22], DPPH molecules can react with both antioxidant or oxygen-active species (AH) (see reaction 1) and radical species (R) (see reaction 2):

$$\mathrm{DPPH^{\bullet}} + \mathrm{AH} \rightarrow \mathrm{DPPH\text{-}H} + \mathrm{A^{\bullet}} \rightarrow \mathrm{A\text{-}DPPH} \quad (1)$$

$$\mathrm{DPPH^{\bullet}} + \mathrm{R^{\bullet}} \rightarrow \mathrm{DPPH\text{-}R} \quad (2)$$

The aim of the present work is to use a DPPH solution to detect the formation of surface free radicals after plasma treatment of black spruce (*Picea mariana*) wood surfaces. Wood samples are first treated using a plane-to-plane DBD operated in He under controlled atmospheric pressure to prevent interactions with ambient air. These results are then compared to those obtained in presence of trace amounts of oxygen in the He plasma to analyze the role of such species on plasma-induced formation of surface free radicals. Selected experiments are also performed on samples exposed to the flowing afterglow of N_2 and N_2/O_2 DBDs open to ambient air under conditions similar to those of Busnel et al. [13].

2. Materials and methods

2.1. Chemicals

Chemicals used in this study were: 2,2-diphenyl-1-picrylhydrazyl (DPPH) (Sigma–Aldrich), ethanol 95% (Commercial Alcohols), helium gas UHP grade (Praxair), methanol ACS certified (Fisher Scientific), methylene chloride ACS certified (Fisher Scientific), nitrogen gas pure grade (Air Liquide), oxygen gas pure grade (Air Liquide).

2.2. Sample preparation

Due to the high reactivity of DPPH with oxygenated functional groups and the porosity of wood that could contribute to increase bulk material reactivity toward the surface, thin, 300 μm-thick black spruce veneers were peeled from a wood plank using a resurfacing Marunaka Tekkosho apparatus model SuperMeca CA-25Y3. To prevent possible extractives reaction with DPPH, some wood veneers were also extracted by the soxhlet-extraction methods with two different solvents, namely ethanol (95%) and methylene chloride [5,23,24]. Both extractions were done over a period of 24 h. In order to avoid outgassing of the samples in the plasma during treatments under controlled He atmosphere (see Levasseur et al. [25]), samples were previously outgassed in a vacuum oven for more than 18 h at 635 Torr and 40 °C. During transport, samples were stored in vacuum bags and left in a vacuum desiccator pumped down using a mechanical pump between experiments.

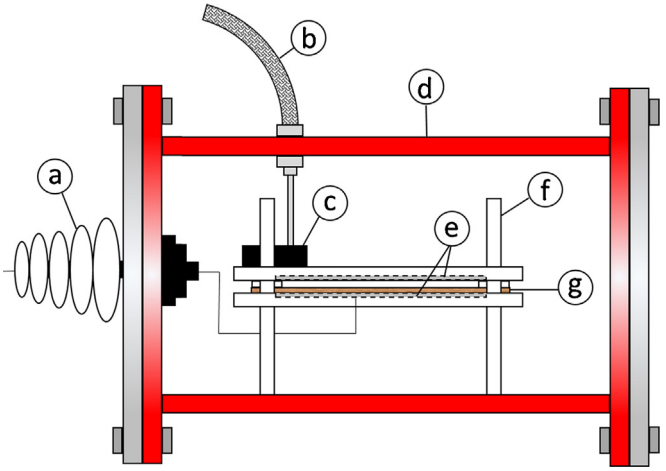

Fig. 1. Schematic representation of the plane-to-plane atmospheric pressure DBD unit with the electrical feedtrough (a) connected to the high-voltage source, the gas input (b), the gas diffuser (c), the aluminum chamber (d) and the two silver-painted alumina electrodes (e) with the bottom electrode acting as the substrate holder for wood samples (g).

2.3. Treatments in plane-to-plane DBD

As shown in Fig. 1, the plane-to-plane DBD system consists of two thin alumina sheets (0.635 mm thick, 70 mm × 115 mm) on which silver-based electrodes (25 mm × 55 mm) are painted. Those electrodes are mounted on a polyoxymethylene sample holder and the top part can be moved up and down in order to insert samples between the two electrodes. Wood veneers (35 mm long by 60 mm wide) are held in place with tape onto a larger solid wood piece to provide mechanical stability and prevent side effects. The discharge gap between the sample and the top electrode is set to 4 mm throughout all experiments. The top electrode is linked to a vacuum feedthrough, which is connected to a high-voltage power supply. The whole system is enclosed in a sealed aluminum chamber evacuated by a mechanical pump to ensure minimal concentrations of air impurities. All experiments are thus conducted under controlled atmospheric-pressure (760 Torr) conditions. The input gases are adjusted by mass flow meters set at 3.0 SLM (standard liters per minute) for He and either 0 (nominally pure He) or 3 SCCM (standard cubic centimeters per minute) for O_2 (He + 0.1% O_2). In nominally pure He, the plasma was sustained by applying a sinusoidal signal of 4.25 $kV_{pk\text{-}pk}$ at 12 kHz whereas in He/O_2 plasmas the voltage amplitude was set to 2.75 $kV_{pk\text{-}pk}$. These voltages were chosen to obtain comparable discharge currents. The treatment time was fixed to 10 min. Based on ref. [26,27], analysis of the current–voltage characteristics has revealed a power absorbed (or dissipated) by electrons in the discharge of 1.3 W (power density of 0.23 W/cm^3) for He plasmas and 0.35 W (power density of 0.06 W/cm^3) for He/O_2 plasmas.

2.4. Treatments in the flowing afterglow of plane-to-plane DBD

The DBD ATMOS (Plasmionique, Canada) unit presented on Fig. 2 consists of two 285 cm^2, water-cooled, quartz-covered metal electrodes separated by 1.4 mm. The system is open to ambient air. In the present work, the plasma was sustained in nominally pure