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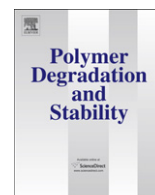
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Short communication

Influence of air plasma treatment at atmospheric pressure on wood extractives

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ABSTRACT

The influence of an atmospheric pressure plasma treatment on wood extractives has been investigated by means of surface energy determination and XPS. Polar and disperse component of the surface energy show only marginal influence of plasma treatment, whereas XPS indicates plasma induced oxidation and degradation of the extractives.

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1. Introduction

In recent years atmospheric pressure plasma (APP) techniques attracted increased research interest in wood modification and were transferred to wood and wood-based materials to improve surface characteristics as wettability or bondability [1–6]. Belgacem et al. [7] and others [8–11] could verify the generation of polar functional groups by X-ray photoelectron spectroscopy (XPS) and surface energy determination on APP treated cellulose, lignin and wood. Moreover, Klarhöfer et al. [12] investigated APP treated lignin and cellulose surfaces by a combination of XPS, ultraviolet photoelectron spectroscopy (UPS) and metastable impact electron spectroscopy (MIES). APP treatment in oxygen containing atmospheres oxidizes the lignin surface by the generation of hydroxyl, carbonyl, and carboxyl groups and reduces cellulose surfaces by the degradation of hydroxyl groups and the formation of double bonds between carbon and oxygen [12]. Although wood extractives only account for approx. 5% of wood mass, they considerably affect surface properties. In particular extractives are the cause of hydrophobic properties of wood surfaces [13–15]. Therefore, this work focuses on the evaluation of the impact of air driven dielectric barrier discharges (DBD) at atmospheric pressure on pure wood extractives by means of surface energy determination and XPS.

2. Materials and methods

Pine sapwood (*Pinus sylvestris*) was extracted with hot water and subsequently with ethanol:cyclohexane (1:2) in a Soxhlet extraction according to Rowell [16]. For contact angle measurement, microscope slides were immersed into the hot water extractive solution and the ethanol:cyclohexane extractive solution, respectively. Subsequently the liquids were vaporised and a layer of the corresponding extractive remains on the microscope slides. For XPS-analysis, a droplet of extractive solution was applied on gold foil, after evaporation of the liquids the residue forms a thin film of the respective extractive on the foil. Contact angles (sessile drop) were measured using a Krüss G 10 measuring system according to the constant wetting rate angle (CWRA) method [17]. Surface energy was calculated according to the approach of Owens and Wendt [18] by averaging contact angle data of 30 droplets (droplet volume = 10 µl) using distilled water, glycerol, ethylene glycol, diiodomethane and formamide [19]. XPS was performed using a commercial X-ray source (Fisons XR3E2-324). The measurement parameters were described in Klarhöfer et al. [20]. The DBD setup and the treatment parameters for plasma treatment of microscope slides were described elsewhere [21]. The extractive coated Au foils were plasma treated by a DBD in the preparation chamber of the XPS apparatus, which was filled with synthetic air to atmospheric pressure. After treatment the chamber was evacuated to a pressure below 10⁻⁸ Pa in order to perform measurements. Accordingly, plasma treatment and measurement were performed *in situ*. The used DBD setup consists of silica glass

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covered electrode. The distance between the sample and the electrode was adjusted to 2 mm. A pulse generator was used as plasma source, providing 18 kV pulses with pulse widths of 0.6 μ s at a repetition rate of 25 kHz. The high voltage supply delivers a power of approx. 2 W. All samples were treated for 2 s. Since treatments of microscope slides and Au foil were performed with the DBD method using virtually equal parameters, it can be assumed that mechanisms and impact of plasma treatment were similar and differ only quantitatively [22].

3. Results and discussion

Fig. 1 depicts the surface energy data of the hot water extracted fraction (water extractives) and the ethanol:cyclohexane extracted fraction (solvent extractives) in untreated and plasma-treated state. Generally it has to be taken into account that the extracted compounds as well as the remaining wood structure behave differently than the original material. With plasma treatment, the initially high polar component of water extractives (approx. 24 mN m^{-1}) increases slightly to a value of approx. 28 mN m^{-1} . The polar component of solvent extractives exhibits no distinct impact of treatment and fluctuates between values of 11 and 4 mN m^{-1} . Whereas for water extractives the disperse component increases, for solvent extractives the disperse component initially decreases followed by an increase after 20 s plasma treatment.

Increased wettability of wood surfaces by plasma treatment was attributed by Sakata et al. [23] to oxidative activation of extractives. In contrast results of this study indicated that water extractives exhibit only slight increase in polar and disperse part of surface energy due to plasma treatment, and solvent extractives show no clear impact of plasma treatment on their surface energetic characteristics. Back [24] proposed oxidative removal of extractives which is supported by results of Wolkenhauer et al. [25] and Vander Wielen et al. [26]. Wood surface characteristics, e.g. wettability and bondability would benefit from degradation and removal of extractives by removing the weak boundary layer and revealing wood main components. The ambiguous results of surface energy determination of plasma treated solvent extractives might be interpreted as removal of extractives revealing the untreated and hence not altered extractive surface. Therefore, untreated and plasma treated surfaces of extractives were

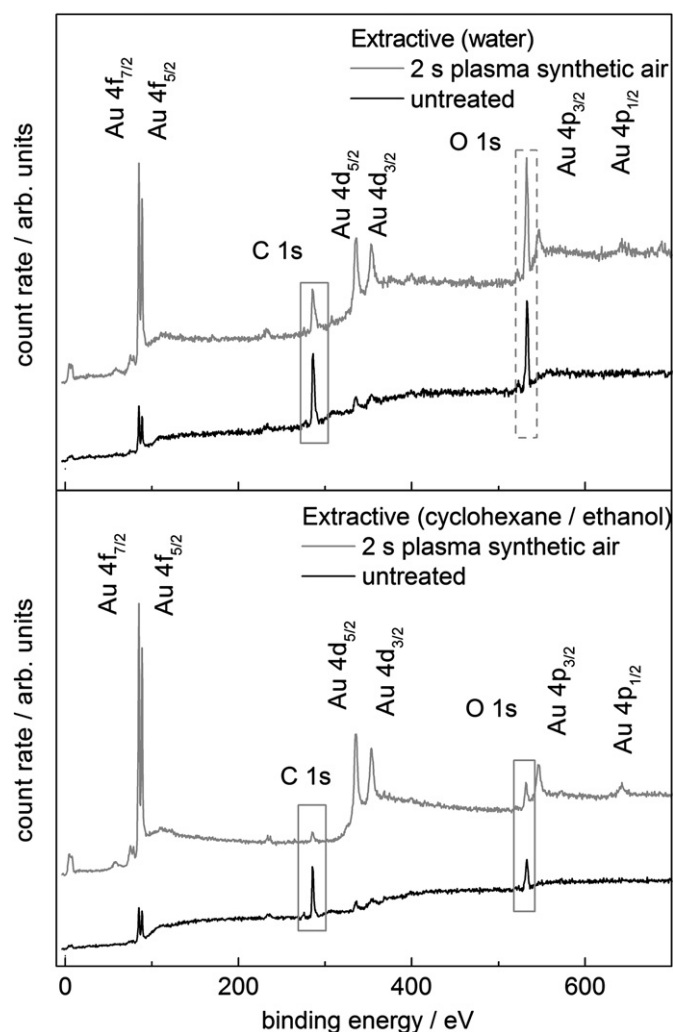


Fig. 2. XPS of untreated and 2 s in air plasma treated extractives of pine wood (water and solvent extractives).

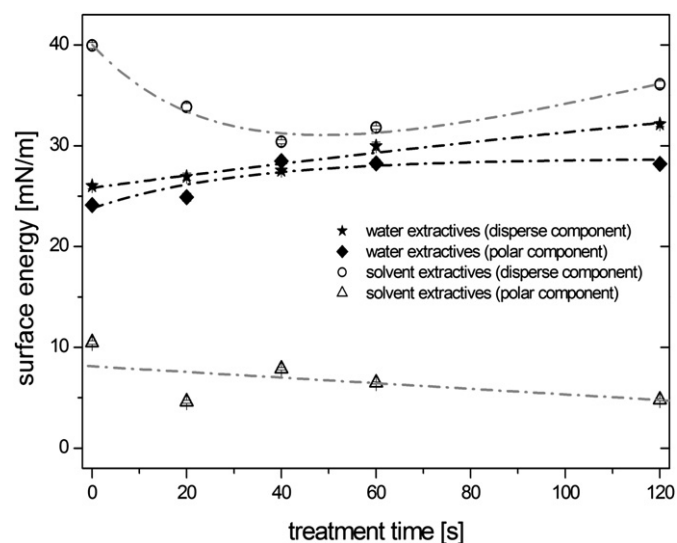


Fig. 1. Polar and dispersive component of surface energy of water extractives and solvent extractives of pine sapwood against plasma treatment duration.

investigated and analyzed by XPS in order to validate whether extractives were degraded or oxidized or both.

Fig. 2 shows XPS spectra of untreated and 2 s in air plasma treated water and solvent extractives. The O/C ratio of the untreated surfaces amounts to 0.39 for the water extractives and 0.19 for the solvent extractives. Air plasma treatment leads to the oxidation of the surface indicated by an increased O/C ratio of 0.75 for the water extractives and 0.49 for the solvent extractives after plasma treatment, supporting the assumption of oxidative activation of the surface mentioned before. Additionally a significant decrease of the C 1s and O 1s signal after plasma treatment for both extractives can be observed. Simultaneously the contributions from the gold substrate increase, clearly indicating the decomposition of the extractives during plasma treatment.

4. Conclusions

Surface energy determination of untreated and plasma treated water soluble and ethanol:cyclohexane soluble wood extractives indicate only a minor impact of plasma treatment on their surface energetic characteristics. By means of XPS an oxidative degradation and the decomposition of the extractives can be shown. The surface energy of the residual oxidized surface of both extractives was

expected to be greater than observed in this study, due to the oxygen enrichment at the surface. These findings indicate that wood extractives were oxidized, degraded and removed by DBD treatment at atmospheric pressure.

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