

MODIFICATION OF WOOD WETTABILITY (EUROPEAN BEECH) BY DIFFUSE COPLANAR SURFACE BARRIER DISCHARGE PLASMA

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In this work, surface activation of European beech wood (*Fagussylvatica*) treated by diffuse coplanar surface barrier discharge plasma (DCSBD) is presented. Plasma activation was performed in air atmosphere. The power of plasma in the treatment was 400 W and exposure times were of 3, 5 and 10 s. The wettability of wood was investigated through the measurement of water droplet contact angle. DCSBD plasma generates a wide range of reactive species in ambient air. These species react with the treated sample surface and provide a convenient resource for surface activation of wood material and its components. DCSBD plasma activation demonstrated that plasma treatment is an effective method for changing the wood surface wettability depending on the surface/electrode distance (from 0 to 1.6 mm). At a distance of up to 0.4 mm, the surface becomes hydrophilic when compared with the untreated sample. On the contrary, if the distance exceeds 0.8 mm, the surface becomes hydrophobic. The hydrophobic effect evolved during storage time.

Keywords: wood, wettability, plasma, diffuse coplanar surface barrier discharge, reactions, reactive intermediates

INTRODUCTION

The need for innovative green chemistry processes for the development of sustainable processes has led to activities in wood and coating chemistry. Physicochemical modification of lignocellulosic material surfaces using low temperature atmospheric plasma is a new developing area of technological research. Substances applied on surfaces are efficient in eliminating the adverse impact of various factors, such as radiation, temperature and oxidants, which directly influence the degradation process and stability of wood surfaces. Over the last few years, there has been an increasing interest in using plasma activation at atmospheric pressure by Diffuse Coplanar Surface Barrier Discharge (DCSBD)¹⁻⁴ as a reinforcing tool providing the desired properties of natural composite materials.⁵⁻²¹

Conventional methods of surface modification, such as chemical treatment, mechanical roughening, and flame treatment suffer from problems of

uniformity, reproducibility and cost effectiveness.²² Plasma surface modification of materials offers a uniform, reproducible, economic and environmentally friendly alternative.²³ Advantageously in comparison with competitive plasma techniques, this plasma source is capable of generating visually uniform “cold” high-power-density diffuse plasma in any working gas, including pure atmospheric-pressure oxygen, without the use of expensive He or Ar. Very high plasma power densities achieving $\sim 100 \text{ W/cm}^3$ allow for short plasma exposure times of the order of 0.1 s and, consequently, high treatment speeds.²⁴ DCSBD is able to create a layer of macroscopically homogeneous, thermally non-equilibrium plasma with a high density of free electrons without any contact with the electrodes when increasing the AC wattage input. The higher the input, the higher the homogeneity of the plasma is. An advantage of the system lies in the high density of the output at a small plasma layer

thickness. The analysis of morphological alterations of polymer material surfaces due to DCSBD plasma impact has shown that typical dimensions of the alterations are of the order of tenths of micrometers. This is why the surface treatment using DCSBD can be termed nanomodification. The effect of the treatment conditions markedly depends on the treatment time, applied power, sample/electrode distance, type of gaseous and construction materials. Plasma surface treatment creates new chemically active functional and cross linking groups on the sample surface. These functional groups are usually of hydrophilic nature. Plasma is also used to improve the ability to adhere to substrates, such as glass, polymers, ceramics, paper, wood and various metals.⁶⁻²⁷

In terms of renewable materials, plasma surface modification of wood and products obtained from raw wood materials, e.g. lignin, cellulose and extractives, is of interest. Dry wood is primarily composed of cellulose (40-50%), lignin (20-30%), hemicelluloses (20-30%) and extractives (3-10%). Although wood extractives only account for approx. 3-10% of wood mass, they considerably affect surface properties. In particular, extractives are the cause of hydrophobic properties of wood surfaces.²⁸⁻³⁰

In the present study, a treatment by DCSBD atmospheric plasma in air was conducted on European beech wood (*Fagus sylvatica*) surface. The aim of this investigation was to study the influence of plasma treatment on wood wettability and to unveil the possible fundamental mechanisms involved in the enhancement of wood surface wettability, described in the literature.

EXPERIMENTAL

Control samples

Samples used in this work: European beech (*Fagus sylvatica*). Wood blocks (30 mm×70 mm×20 mm) were cut from the heartwood of straight grained and defect-free boards and conditioned for several weeks at 24 °C and 50% relative humidity to bring the moisture content to 8% prior to plasma modification. The European beech wood used in this study had the following chemical composition: 47.5% cellulose, 23.7% hemicelluloses, 25.6% lignin, 1.3% ash and 1.9% extractives (hot-water extract).

Preparation of samples

Samples were rubbed by sandpaper with size 150 of grain fractions before the treatment. High-density wood must have growth rings that together with the tested area

have the angle close to the value of 45 degrees. Angles smaller than 45 degrees can cause the delamination of wood, which makes the samples unsuitable for investigation.

Conditions of plasma modification

Plasma treatment of wood samples was done by Diffuse Coplanar Surface Barrier Discharge – planar source of the low-temperature plasma. The DCSBD electrodes, consisting of 15 pairs of silver strip like electrodes embedded 0.5 mm below the surface of 96% Al₂O₃ ceramics, were energized by an HV generator LIFETECH VF 300. The mutual distance between the 200 mm long and 2 mm wide silver strip electrodes was 1 mm.^{26,27} The distance between the sample and the electrode was varied in the range 0-1.596 mm by spacer plates (0, 0.13, 0.27, 0.4, 0.53, 0.67, 0.8, 1.06, 1.6 mm). The thickness of a plate was 0.133 mm. To measure the effect of plasma, a DCSBD system with a magnitude of 400 W was used. The used equipment was described elsewhere.²⁰ The time of plasma modification was set to 3 s, 5 s, and 10 s. Ambient air was used as working atmosphere.

This work describes the effects of the distance between the treated surface and the electrode surface on wood surface wettability.

Contact angle

To express the impact of surface modification for specific sample/electrode distance, the changes of contact angle for water were monitored and detected as a change of surface wetting. Distilled water with pH = 7 was used. Measurements were performed in accordance with the procedure described by M. Ondraskova *et al.*,²⁰ applying a SEE System device (Surface Energy Evaluation System) equipped with a CCD camera. A 50 µl water droplet was put on the surface and its uptake time was measured. An image analysis system calculated the contour of the drop from an image captured by means of a video camera. Ten measurements of contact angle were taken for statistical evaluation. The results provided here are average values of the measurements.

Storage time

The samples were exposed to plasma for 5 seconds. Contact angles of samples were measured 0, 72 and 120 hours after the plasma treatment. The time elapsed since the plasma treatment is expressed in this case as the storage time under the given conditions. After the plasma treatment, the samples were kept in a conditioned chamber at RH = 54.1% and T = 23.3 °C. The contact angle was measured 10 times for each sample and the average value plus standard deviation was calculated. The contact angle of untreated native wood (control) sample was 60.4 ± 3.7°.

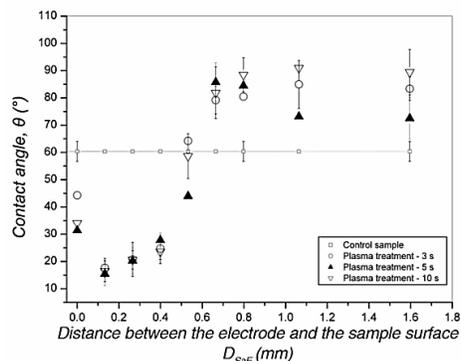


Figure 1: Contact angle variation (θ , °) as a function of the distance between the electrode and the sample surface (D_{SaE} , mm) (the line represents the untreated control sample of wood (European beech (*Fagus sylvatica*)))

RESULTS AND DISCUSSION

The investigation of the influence of plasma treatment on the surface of materials is a very prolific research area, which has attracted the interest of several research groups. The results obtained in the present study are compared with those reported by other groups. A purposeful surface modification is conditioned by the control of materials inner structure (changes of functional groups), which can be achieved through wettability changes due to plasma treatment. The results of our work, presented in Fig. 1, are consistent with those obtained by other authors. To assess the effect of plasma treatment (treatment time of 3, 5, or 10 s) as a function of the sample/electrode distance, the contact angle for water was followed. Based on the values obtained, the hydrophilicity and hydrophobicity of the treated wood samples were evaluated and compared with those of the reference untreated sample.

For the untreated wood sample, the contact angle was $60.4 \pm 3.7^\circ$. A decrease in this angle due to the treatment is an evidence of an increase in hydrophilicity. From the practical point of view, it means that plasma treatment leads to changes in the wood surface properties, which can be useful for, e.g., better penetration of water-based paints applied to the surface. Irrespective of the time of treatment, in the distance interval from 0 to 0.34 mm the contact angle decreased. Application of plasma for 5 s at a distance of 0.53 mm leads to higher hydrophilicity of the sample (see Fig. 1). At 3 s treatment the contact angle is $64.2 \pm 4.1^\circ$, revealing a slight increase when compared to the contact angle value of the untreated wood surface. It means that the nature of the surface changes and

its wettability reduces. When increasing the distance over 0.67 mm, the contact angle increases for all treated samples, as a result their surface becomes hydrophobic (less wettable).

As presented in Fig. 1, along with the distance, wettability is influenced by the time of the treatment. These results are in full agreement with those reported in other studies.^{20,27} It is obvious from Fig. 1 that after 3 s of treatment the treated surface becomes hydrophilic for a distance of up to 0.4 mm. On the contrary, at a distance of 0.53 mm and higher, the wood surface becomes hydrophobic as based on the contact angle increase. Further gradual increase in the distance causes a gradual increase of the contact angle, i.e. hydrophobicity of wood. The highest hydrophobicity was registered for a distance of 1.06 mm, when the contact angle reaches the value of $84.9 \pm 8.8^\circ$, which represents an increase by 40.7%, compared to the value for the untreated wood surface. At even higher distances the contact angle slightly decreases, maintaining, however, the value $83.4^\circ \pm 4.3^\circ$. The wettability of wood treated for 3 s thus does not depend significantly on the distance. After 5 s of treatment at 0.67 mm distance, the contact angle increased by 42%, when compared to the untreated sample. Further distance increase leads to a decrease in the contact angle, reaching $72.5 \pm 7.6^\circ$ at 1.6 mm, higher by 20.1% than the contact angle value for the untreated sample. Within the distance range from 0.67 mm to 1.6 mm, the wood surface sample exhibits still a higher hydrophobic character than that of the untreated sample. Plasma treatment lasting 10 s causes an increase in hydrophilicity in the distance range from 0 to 0.53 mm. On the contrary, in the range from 0.67 to 1.6 mm, the

treated sample surface becomes hydrophobic. At the surface/electrode distance ≥ 0.8 mm, the average contact angle is $89.6^\circ \pm 1.3^\circ$.

DCSBD treatment is effective in improving wood wettability, but it can also be used to obtain better wood resistance against water. This can be a new technique for protecting wood against water, thus applicable to wood used outdoors.

From the chemical viewpoint, the explanation is that under plasma treatment some polar and oxygen-containing groups (e.g. hydroxyl, carbonyl, carboxyl, ether, etc)^{23,31,32} are introduced, thus changing the polar character of the wood surface and increasing hydrogen bonding capabilities. Carboxylic end groups are oriented towards the surface, leading to the exposure of dispersive linkage groups at the surface, and it may possibly be an explanation for the change/decrease in wettability.³³

The formation of acidic groups due to exposition to DCSBD plasma has been proved in several papers,^{20,26,34,35} demonstrating that plasma treatment results in a pH decrease with the increase of wood surface/electrode distance. For pine tree (*Picea alba*), pH decreases from 6.2 to 4.2, for beech from 5.8 to 3.7 and for oak from 4.7 to 3.7.^{34,35}

On the other hand, the components of wood, such as lignin macromolecules or polysaccharide matrix, are also cross-linked (up to a few microns), which leads to an increase in scratch resistance and to an improvement in the barrier properties of the wood material and the production of some new contact sites on veneer surfaces.^{36,37}

Actually, only a few basic investigations have been carried out so far to understand the chemistry involved in the plasma treatment. One way to approach this phenomenon is to investigate the effect of the generated species on the chemical structures likely to be present in the process. A lot of research has already been carried out on the degradation mechanism of lignin, cellulose, hemicelluloses and extractive compounds in the presence of ozone, oxygen and hydroxyl radicals and other reactive species emerged in the bleaching and delignification of pulp and wood.

The effect of DCSBD plasma on chemical changes is quite complex and has not been fully explained so far. One of the reasons may be that different kinds of atmosphere may give rise to different kinds of radicals and specific cations (N^+ , O^+ , OH^+ , H_2O^+ , N_2^+ , O_2^+ , Ar^+ , N_2O^+ , CO_2^+) depending on the used plasma output. This

influence of plasma output on the radical formation was found in the work by Lazovic *et al.*,³⁸ where the authors observed that in air atmosphere, the increase of the plasma output from 300 W to 400 W resulted in an increase in the concentration of N^+ and O^+ radicals, while that of NO^+ decreased. In addition, plasma also contains other gases, e.g. NO_2 and O_3 . Simek and Homola³⁹ determined the efficiency of ozone formation by DCSBD in dry synthetic air in a wide range of applied energy densities (0.01-1 Wh/l), and airflow rate (5-50 l/min). At the mentioned parameters, the production of ozone was 800 ppm, i.e. 5 g/h (which represents 40 g/kWh). The production of ozone depended on the type of coated ceramic, e.g. TiO_2 ceramic produced more ozone than pure Al_2O_3 .

It is just the formed ozone that can play an important role in the reactions with individual components of wood (lignin, hemicelluloses, cellulose). The destruction of the aromatic ring of lignin has been recognized, while the process of ionization itself depends on the type of lignin as well as the environment in which the ozonization is performed. The formation of new compounds with active oxygen, peroxides, and hydroperoxides was also proved.⁴⁰ Ring opening and the resulting introduction of carboxyl groups on the lignin moieties offer a reasonable explanation for the change of lignin properties or the formation of new chromophores. These compounds are active and capable of other reactions with the lignin structures, e.g. C=C fission reaction or radical reaction initiations.⁴¹ In the oxidation of lignin, it is possible to assume a similar oxidation mechanism that has certain peculiarities, due to both the macromolecular character of lignin and its complex structure. A relatively slowly moveable lignin macro matrix lowers the possibility of recombining the radicals formed during oxidation to such an extent that a certain part remains alive even after the oxidation is completed.⁴¹

The proposed reaction mechanism of lignin compounds with ozone has been mentioned in different studies.⁴⁰⁻⁵⁷ The elementary steps of the mechanism for this reaction may involve:

- electrophilic substitution and 1,3-dipolar insertions;⁴²
- oxidative cleavage of C=C;⁴³
- syn-anti zwitterion isomerization;⁴⁴
- Criegee rearrangement;⁴⁵
- dimerization and polymerization via diperoxides and polymeric peroxides;^{43,44}

- cleavage of the carbon-carbon bonds of aromatic ring via 1,3 dipolar cycloaddition;⁴²
- electrophilic substitution on aromatic rings^{46,47} resulting in hydroxylation and quinone formation;
- attack at a carbon-hydrogen bond adjacent to a 1,3 dipolar insertion to hydrotrioxide;⁴⁸
- cleavage between the ring carbons bearing the hydroxyl and methoxy substituents;⁴⁹
- oxidative radical coupling involving the phenoxy radical condensation of phenolic compounds during the first time of ozonisation;⁴²
- autoxidation of lignin initiated by ozone.⁴⁵

In reactions with lignin and cellulose, ozone behaves as a highly selective reactant, which can be documented by the values of the corresponding rate constants, reaching $\sim 10^4 \text{ M}^{-1}\cdot\text{s}^{-1}$ when reacting with lignin compounds and $\sim 10^{-1} \text{ M}^{-1}\cdot\text{s}^{-1}$ in reactions with carbohydrate type substances at pH 2. Stemming from the rate constant ratio,⁵⁰⁻⁵² it can be concluded that the selectivity of ozone reactions ranges between 10^5 - 10^6 .

Given the selectivity dependence on pH, it can be supposed that ozone reacts predominantly with lignin during plasma treatment. This hypothesis is based on the acidic character of the reaction media stabilizing ozone against its decomposition. Due to plasma treatment, acid components (formic acid and acetic acid) are formed, the wood surface becomes more acidic which, in turn, leads to increased selectivity of ozone reactions with wood components. The mechanism and reaction types in lignin reactions are known and described in several papers.⁵³⁻⁵⁵ Several studies on the action of plasma treatment on fibre bound lignin, wood and on low molecular weight lignin model compounds have been reported.^{56,57}

Plasma primarily creates phenolic hydroxyl groups and forms the corresponding radicals.^{58,59} Studies published in 1993, 1995, 2005, 2010 and 2008 demonstrated that Ar plasma treatment of fibers led to modification of the lignin chemical structure and to the creation of new radical species, largely of phenoxy radicals.⁶⁰⁻⁶⁴

The impact of ozone on cellulose degradation was investigated on various model compounds of polysaccharides and cellulosic materials along time before 1966⁶⁵ and later.⁶⁶⁻⁶⁹ Cellulose degradation is caused by a number of reactions initiated by formed hydroxyl (free) radicals.⁵⁵ These radicals originate from reactions of ozone with lignin. Free

radicals in lignin are formed mainly by the cleavage of ether bonds leading to phenoxy radicals, but alkoxy radicals can also be produced when chemical bonds in the lignin-carbohydrate complex are broken.⁷⁰

It is obvious that along with ozone reactions, during plasma treatment, reactions of other radical species, such as hydroxyl radicals, also occur, however with lower selectivity, i.e. both with lignin and carbohydrates. In general, the hydroxyl radicals react rapidly with most organic compounds. Their reactions with alkenes, aromatics, and carbohydrates are very fast, with second order rate constants⁷¹ in the range of 10^9 - $10^{10} \text{ M}^{-1}\cdot\text{s}^{-1}$. According to the literature,⁷² the corresponding selectivity of the hydroxyl radical seems to be only about 5. Reactions of plasma result in changes in the wood surface character, expressed as changes in surface wettability due to the formation of various functional groups on lignin, carbohydrates, or the formation of extractives. Electron Spectroscopy for Chemical Analysis (ESCA) is a frequently employed technique that can detect changes in the surface chemistry of materials. Belgacem *et al.*⁷³ and others^{74,75} verified the generation of the mentioned functional groups, such as aldehyde/ketone and carboxylic acid groups, by ESCA on plasma treated cellulose, lignin and wood. These results were confirmed by Calvimontes *et al.*⁷⁶ According to the ESCA measurements, plasma reactions changed the surface chemistry by decomposition of polymer chains and oxidation reactions, forming aldehyde and carboxylic acid/carboxylate groups. A plasma treatment increased the relative amount of oxygen in the sample surface of cellophane foils.⁷⁷ The results of ESCA⁷⁷ may indicate that dielectric-barrier discharge treatment leads to oxidative reactions along with surface cleaning. Increased wettability of wood surfaces by plasma treatment was attributed by Sakata *et al.*⁷⁸ to oxidative activation of extractives. Oxidative removal of extractives is supported by the results published by Van der Wielen *et al.* and Wolkenhauer *et al.*^{77,79} This effect of plasma treatment was confirmed in the work of Avramidis *et al.*³⁰ The applied plasma processes generate a wide range of reactive species in the treated system, which undergo consecutive chemical reactions, thus creating several oxygen based functionalities at the interface (carbonyl, carboxyl, ether, peroxides etc.). Some examples of activation of different materials are reported in the literature.⁸⁰⁻⁸⁵

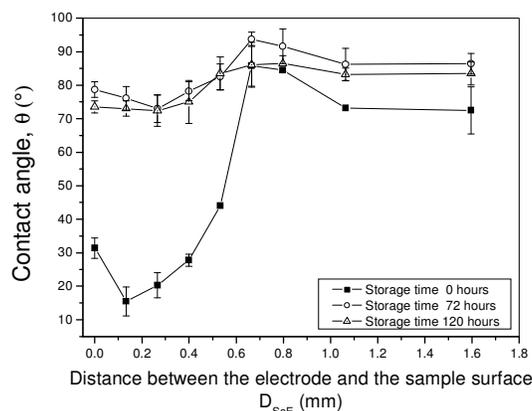


Figure 2: Effect of storage time after plasma treatment (0, 72 and 120 hours); plasma treatment time of 5 s, atmosphere – air

Fig.2 presents the dependence of sessile contact angle on the distance between the electrode and the sample surface D_{SaE} (mm); the contact angle was measured after 0, 72 and 120 hours from 5 s lasting plasma treatment. The contact angle for the untreated beech wood sample was of 60.4° . The sample measured right after the plasma treatment showed a dramatic decrease of the contact angle value approximately down to 15° for the mutual distance set to 0.13 mm (1 glass cover slide), being considerably lower for all distances from 0 to 0.5 mm than the value for the reference sample. In this case, a hydrophilization effect occurred. However, when the samples were stored for 72 and 120 hours, a hydrophobization effect was observed for all the samples and contact angles reached values from 70° to 95° . A stronger hydrophobization effect was remarked on the samples stored for 72 hours, while those stored for 120 hours showed a further small decrease of contact angles. The information on the impact of storage time is important for the potential use of plasma treatment. During the storage time, the activated surface of the wood further reacted with the surrounding environment (recontamination of the activated chemical groups on the wood surface), which was reflected upon the change in the contact angle. The results thus obtained are relevant especially for the application of waterborne coating systems, allowing to conclude that it is appropriate to apply coating systems right after plasma treatment to take advantage of the potentially best hydrophilization effect in order to achieve the best bonding between the activated wood surface and the applied coating.

CONCLUSION

DCSBD plasma treatment in the air is advantageous as it is an efficient, clean alternative for modifying wood surfaces. Such a treatment is effective in improving wood wettability, but can also be used to decrease it in order to make wood surface waterproof. This can represent a new way of protecting wood against water, in particular, for outdoor uses of wood.

Previously reported results indicate that plasma treatment leads to different reactions among the components of wood. Plasma activates the surface of wood and its lignin carbohydrates and extractive compounds react on several sites via a number of mechanisms. DCSBD plasma in air generates reactive intermediates, such as O_2^+ , 1O_2 , O_3 , O , O^+ , O , ionized ozone, free electrons, OH , N , CO_2 , excited states of N_2 , etc. These species react with the wood surface and provide a convenient resource for its activation, and purposeful alteration of its wettability.

The results of the present study on the DCSBD plasma activation of *Fagus sylvatica* demonstrate that the plasma treatment is an effective method in changing wood wettability. Compared with the untreated samples, when applying plasma at a wood surface/electrode distance of up to 0.399 mm, the wood adopts a hydrophilic character for all used times of plasma treatment, while at a distance over 0.798 mm, the wood wettability decreases.

Due to the impact of the ambient atmosphere, the properties of plasma treated surfaces are changed and the surfaces become more hydrophobic. A hydrophilic surface becomes hydrophobic when compared to an untreated

surface. Such a hydrophilic surface is more reactive in air atmosphere than a hydrophobic surface.

The results obtained in this study are relevant especially for the application of water-borne coating systems, leading to the conclusion that it is appropriate to apply coating systems right after the plasma treatment, when the activated wood surface adopts the highest degree of hydrophilicity.

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