

Effect of DCSBD plasma treatment on surface properties of thermally modified wood.

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The focus of this study was to characterize the surface changes of several thermally modified wood species after treatment with diffuse coplanar surface barrier discharge (DCSBD). Surfaces were characterized before and after DCSBD plasma treatment of varying time by applying scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and contact angle measurements to determine the surface free energy. An asymptotic increase of surface free energy up to 63- 64 mJ/m² was observed for all thermally modified wood species already after 5 and 10 s of plasma treatment. This increase could be attributed to the increase of the polar component of surface free energy. XPS measurements revealed that the O/C ratio of oxygen to carbon atoms increased from 0.2- 0.3 before plasma treatment up to 0.7- 0.8 after plasma treatment. A linear correlation was found between the surface free energy and O/C ratio of thermally modified wood before and after plasma treatment. SEM imaging revealed that on the micrometer scale the surface morphology did not change after plasma treatment. However, nanoscale structures were observed at higher magnification after 60 s of DCSBD plasma treatment.

Keywords: atmospheric pressure plasma, DCSBD, thermally modified wood, plasma surface modification, surface energy, surface chemical composition

Thermal modification of wood is an environmentally friendly process that has received considerable applied research interest over the past decades [1]. During thermal treatment the chemical composition of both the wood bulk and surface changes [2]. The main advantages of thermally modified wood are reduced water absorption [3], increased dimensional [4] and biological stability [5,6] and resistance to weathering [7]. Thermally modified wood exhibits reduced surface free energy [8] leading to reduced wetting with polar liquids [9,10]. It is

caused by the decrease of the O/C ratio of oxygen to carbon atoms on the surface [9]. This has been shown to negatively affect adhesion of coatings and resins [11].

Atmospheric pressure non-equilibrium non-thermal plasmas suitable for surface modification are typically generated in dielectric barrier discharge (DBD) arrangements powered by alternating high voltages of frequencies of up to a few tens of kHz [12]. The diffuse coplanar surface barrier discharge (DCSBD) configuration has been shown to be especially suitable for surface treatment of various materials such as polymer films [13], glass [14], textiles [15], wood [16] and plant seeds [17]. The main advantage of the DCSBD for surface treatments are the relatively low applied voltages, the high energy density [18] and efficiency [19].

The effect of plasma on surfaces is brought on by the concurrent reactions of numerous excited and ionized gas phase species, radicals and UV radiation. The plasma modification of wood affects only the properties of a thin surface layer and does not change the bulk properties [20]. To date plasma treatment of thermally modified wood has only been investigated in a few studies which demonstrated improved absorption characteristics and increased surface energy after plasma treatment [21–23]. Recently it was shown that the polar part of surface free energy of thermally modified wood surfaces increased considerably after DBD plasma treatment. It was affected by the treatment time, thermal modification temperature and wood species genus [24]. The increased surface free energy was attributed to an increase of the ratio of oxygen to carbon atoms on the surface after the plasma treatment.

A broader study comparing different thermally modified wood species would provide a deeper insight into plasma treatment of thermally modified wood surfaces. The aim of the present study was to investigate the effect of DCSBD plasma treatment on a range of thermally modified wood species. The combination of surface free energy measurements together with surface chemical composition analysis with X-ray photoelectron spectroscopy and surface morphology characterization with scanning electron microscopy provides detailed information about the surface of thermally modified wood after plasma treatment. The correlation between the surface free energy and chemical composition was investigated.

Experimental

Thermally modified wood samples

The wood samples studied in this work were obtained from the wood competence center TSENTER in Estonia. Thermally treated pine (*Pinus silvestris*), radiata pine (*Pinus radiata*), black alder (*Alnus glutinosa*) and European ash (*Fraxinus excelsior*) had been treated in an autoclave at a maximum temperature of 180 °C and grey alder (*Alnus incana*) and aspen (*Populus tremuloides*) at a maximum temperature of 160 °C. The samples (40×20×90 mm³

radial-tangential-longitudinal) were kept at room temperature and relative humidity of 30-40% and the radial-longitudinal cut was investigated in all experiments described below. Smaller samples (10×3×15 mm radial-tangential-longitudinal) were used for XPS and SEM experiments. Ash wood has a distinct ring-porous structure [25] and specifically the ash latewood part with no pore was investigated while for other species no distinctions were made between the early- and latewood.

Plasma treatment set-up

Diffuse Coplanar Surface Barrier Discharge (DCSBD) is a type of surface dielectric barrier discharge [12] generating a macroscopically quasi homogenous diffuse layer of plasma at atmospheric pressure [26]. The temperature of the treated material does not rise above 35°C with treatments up to 9s [27].

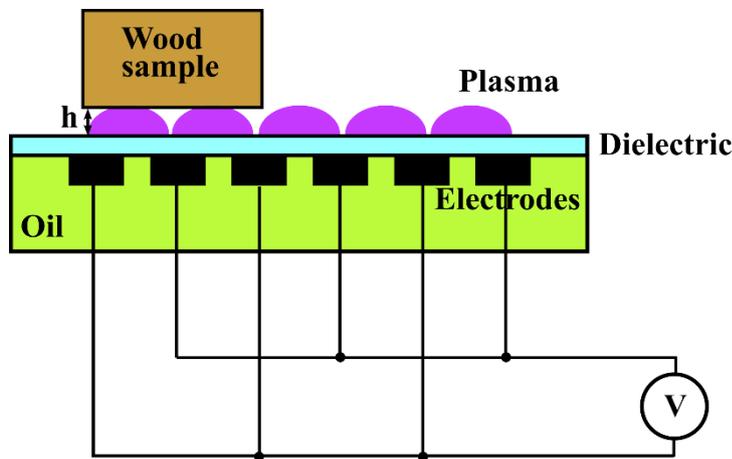


Figure 1. Schematic of the DCSBD setup.

The experimental setup is shown in the figure 1. The electrode system of DCSBD consists of 32 parallel strip-line silver electrodes (1.5 mm wide, 220 mm long and 1 mm strip to strip) embedded in 96% alumina ceramics. In all experiments the DCSBD was operated in air and the electrode system was powered by AC voltage of 15 kHz frequency with a peak-to-peak voltage of 20 kV. The DCSBD unit was cooled by an oil system. The effective area of DCSBD plasma layer was 8×20 cm. During the experiments the input power was monitored and fixed at 400 W which results in approximately 400 W input into the plasma [26]. The plasma treatment time was varied in range of 5- 60 s.

The thickness of the active plasma layer in DCSBD device used is approximately 0.3 mm [26]. In a previous work varying the distance between the treated wood surface and the DCSBD device from 0 to 0.3 mm, no impact on the uptake time of water droplets was observed [16]. However, in this work it was found that the standard deviation of contact angle of water droplets increased when the treated sample was placed directly on the DCSBD

device so the treatment distance was fixed at $h= 0.1- 0.2$ mm in all experiments. During plasma treatment the wood samples were placed on the DCSBD device and moved back and forth to ensure a homogenous treatment.

Surface free energy determination

The indirect determination of the surface energy of a solid surface is based on the Young's equation (Eq. 1)

$$\gamma_L \cdot \cos\theta = \gamma_S - \gamma_{SL} \quad (1)$$

where γ_L is the surface tension of the liquid, θ is measured contact angle of the liquid on the solid surface, γ_S is the surface energy of the solid and γ_{SL} is the interfacial tension between the liquid and the solid. According to the model originally proposed by Owens [28] the total surface free energy of the solid consists of the dispersive component (γ^D) and the polar component (γ^P). The interfacial tension between the liquid and solid can be evaluated by the geometric mean equation (Eq. 2).

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\sqrt{\gamma_S^D \gamma_L^D} + \sqrt{\gamma_S^P \gamma_L^P}) \quad (2)$$

Combining equations (1) and (2) and rearranging according to the linear regression $y=mx+b$ leads to (Eq. 3)

$$\frac{(1+\cos\theta)\cdot\gamma_L}{2\sqrt{\gamma_L^D}} = \sqrt{\gamma_S^P} \cdot \sqrt{\frac{\gamma_L^P}{\gamma_L^D}} + \sqrt{\gamma_S^D} \quad (3)$$

The dispersive (y axis intercept= $\sqrt{\gamma_S^D}$) and polar part (slope= $\sqrt{\gamma_S^P}$) of the surface energy can be determined by measuring the contact angle of a minimum two liquids with known values for polar and dispersive parts of surface tension.

The three liquids that were used in this study are distilled water ($\gamma^D=21.9$ mN/m, $\gamma^P=51$ mN/m), ethylene glycol ($\gamma^D=29$ mN/m, $\gamma^P=19$ mN/m) and diiodomethane ($\gamma^D=50.8$ mN/m, $\gamma^P=0$ mN/m) [29] Contact angles were determined from 1 μ l droplets using the Surface Energy Evaluation System (Advex Instruments, Czech Republic). Contact angles were determined when the droplet stopped spreading on the wood surface and the wetting rate became constant ($d\theta/dt=\text{const}$) [30]. The contact angle values were determined directly from images taken with the CCD camera. The average values of contact angle from measurements of 20 droplets were used for the surface free energy calculation of both plasma treated and untreated thermally modified wood surfaces. The surface free energy was determined within one hour after plasma treatment.

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250Xi (Thermo Fisher Scientific, East Grinstead, United Kingdom). An X-ray beam with

power of 200 W (650 μm^2 spot size) was used. The survey spectra were acquired with a pass energy of 50 eV and a resolution of 1 eV. High-resolution scans were acquired with a pass energy of 20 eV and a resolution of 0.1 eV. To compensate for charges on the surface, an electron flood gun was used. Spectra were referenced to the hydrocarbon type C1s component set at a binding energy of 284.8 eV. Spectra calibration, processing and fitting routines were done using Avantage software.

Scanning electron microscopy (SEM)

The surface morphology was studied by scanning electron microscope MIRA3 from TESCAN (Brno, Czech Republic). To achieve better visualization and prevent charging, the samples were covered by 20 nm Au-Pd composite layer. All samples were measured using secondary emission mode at 5 kV.

Results and discussion

Surface free energy

Figure 2 depicts the measured surface free energy dependence on the plasma treatment time for thermally modified pine (Th-P), thermally modified alder (Th-Al), thermally modified dark alder (Th-Al2), thermally modified ash (Th-Ash) and thermally modified aspen (Th-Asp). The surface free energy of reference samples with no plasma treatment are depicted as Ref. The measurement uncertainty is given as the standard deviation which was calculated for the slope and intercept of the linear regression.

Before the plasma treatment the thermally treated wood samples have varying surface free energies before plasma treatment ranging from 33 mJ/m^2 for latewood of thermal ash (no pores) to 55 mJ/m^2 for thermal aspen. Those differences can be explained by the different heat treatment temperature and variation in wood species [31]. After 5 and 10 s of plasma treatment the surface free energy of all species increased to a similar value of 60- 65 mJ/m^2 which increased only slightly when the plasma treatment time was increased up to 60 s. The reference surface free energy for thermally modified radiata pine (Th-RP) was 42 mJ/m^2 . Already after the 5 s of plasma treatment a complete wetting occurred, i.e. the free surface energy was too high to be measured by the contact angle method.

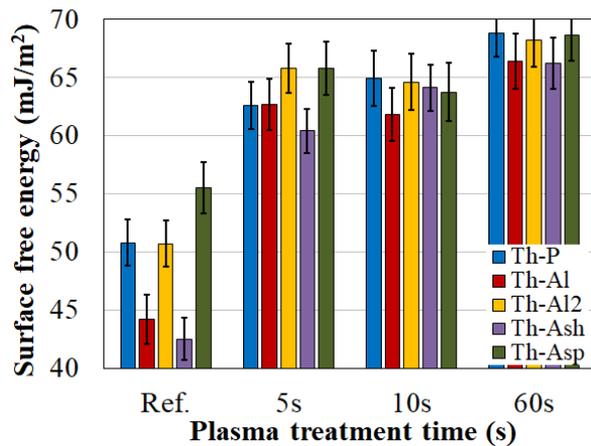


Figure 2. Surface free energy dependence on plasma treatment time for various thermally modified wood species. Measurement uncertainty is given as the standard deviation.

Figure 3 depicts the polar (left) and dispersive (right) parts of surface free energy as a function of plasma treatment time for the investigated thermally treated wood species. Within the experimental uncertainty the DCSBD plasma treatment has no effect on the dispersive part of thermally modified wood. On the other hand, a significant increase of the polar part can be observed after 5 and 10 s of plasma treatment. Treatment time longer than 10 s has little to no further effect on the polar part of surface energy. Thus, in agreement with findings of [24] the increased surface free energy of TMW can be attributed specifically to the increase of its polar component.

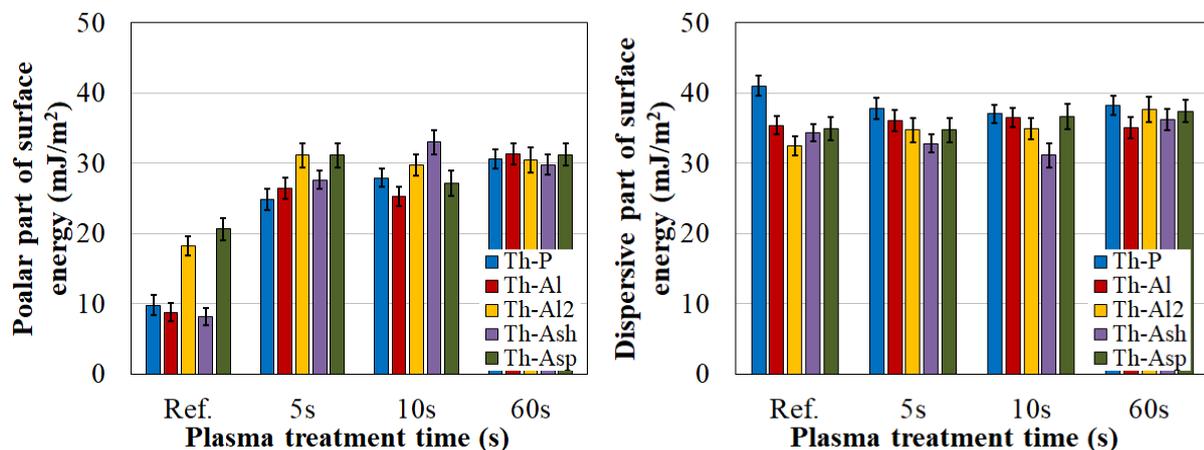


Figure 3. Polar (left) and dispersive (right) part of surface energy dependence on plasma treatment time for various thermally modified wood species. Measurement uncertainty is given as the standard deviation.

Several authors have observed the asymptotic increase of surface free energy of heat treated [21] as well as normal wood [32] surfaces with plasma treatment time. The surface free energy of heat treated *Larix gmelinii* increased to a value of 65mJ/m² as after 10- 20 s of

plasma treatment with an atmospheric pressure plasma jet [21]. This is similar to what was measured in this study for plasma treatments of 5- 60 s.

In the already mentioned work of [24] the DBD plasma treatment of thermally modified beech, pine and spruce increased the surface free energy to similar values of 55- 65 mJ/m² depending on the previous heat treatment temperatures, plasma modification duration and wood species genus. The increased total surface free energy was shown to be due to increased polar part similarly to what was observed in the present study. However, the dispersive part of surface energy was observed to decrease for all investigated species during the plasma treatment which was not seen in this work. A possible explanation could be the different wood species under study or the different plasma device employed for the treatment.

Additionally, aging tests were carried out with thermally modified pine and dark alder after 10 s of plasma treatment. Surface free energy was measured during a period of 14 days after the plasma treatment. The decrease of surface free energy was measured to be less than 15% which occurred within the second week (data not shown).

Surface chemical composition

Figure 4 shows the high-resolution scan of the C1s spectrum together with the fits of the different carbon component used for the deconvolution of the C1s band. The different components of the C1s signal can be assigned to various functional groups according to the number of bonds with oxygen atoms [2]. The C1 peak corresponds to C-C and C-H bonds, the C2 peak corresponds to C-O bonds, the C3 peak corresponds to either O-C-O or C=O group and the C4 peak corresponds to O=C-O groups. These groups are present in different wood constituents [24]. The main contribution to the C1 peak comes from lignin and extractives while C2 and C3 peaks arise from functional groups in lignin and polysaccharides and the C4 peak was attributed to hemicellulose [24].

Figure 4. High resolution XPS spectrum of the C1s band of thermally modified ... after ...s of DCSBD plasma treatment in air.

Table 1 summarizes the data from XPS measurements. The O/C ratio together with the deconvoluted components (at%) of the C1s spectra are given for the investigated thermally modified wood species after the plasma treatment. XPS spectra of thermally modified pine could not be measured due to increased charging of the surface.

The O/C ratio increase asymptotically with DCSBD treatment time for all investigated species. The initial (not plasma treated) values ranging from 0.19- 0.32 increased to 0.7- 0.83

after 60 s of plasma treatment which is comparable with an O/C ratio of 0.72 reported for thermally modified beech after DBD plasma treatment [24].

The changes in the C1s components are not as pronounced as in the O/C ratio but a short duration (5- 10 s) plasma treatment clearly decreased the C1 component and increased the C2, C3 and C4 components. The somewhat higher initial at% values measured for the C1 component compared to those reported by Altgen et al [24] could be due to increased amount of extractives on the surface resulting from the relatively lower thermal treatment temperatures [33]. Noteworthy is that the at% of the C1 component decreased after 5 s of plasma treatment but for all investigated species it increased somewhat when the treatment time was extended from 10 to 60 s. The possible explanation could be the relative increase of lignin on the surface due to the degradation and removal of low molecular weight extractives during plasma treatment as reported previously [34].

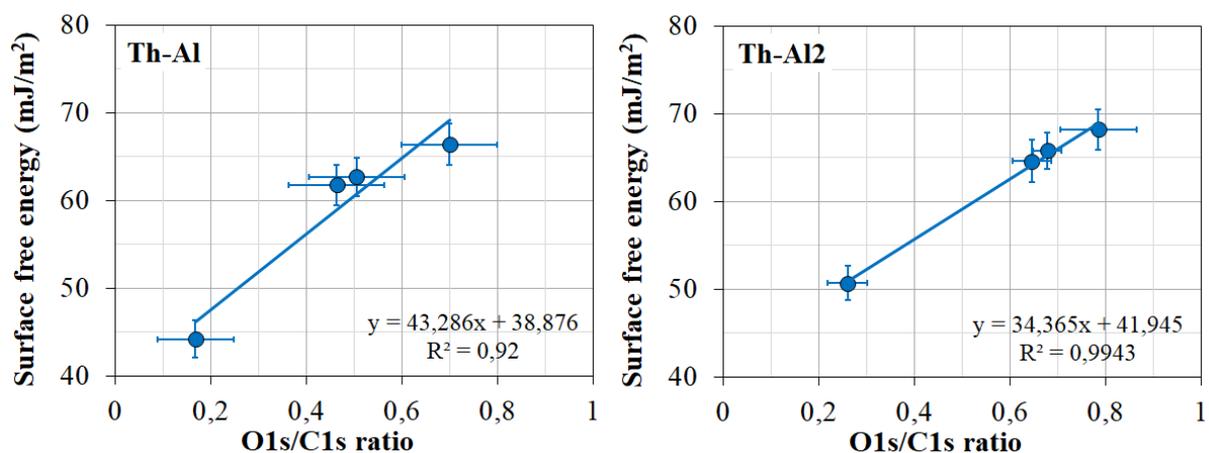
Table 1. XPS data for the O/C ratio and the components (at%) of the deconvoluted C1s spectra of investigated thermally modified wood samples after DCSBD plasma treatment.

Treatment time (s)	Thermally modified alder				
	O/C	C1	C2	C3	C4
Ref.	0.19(0.08)	84.7(1.3)	8.9(0.9)	2.7(0.7)	3.7(0.9)
5	0.5(0.1)	46(4)	27.2(2.4)	11.9(1.9)	14.7(1.9)
10	0.46(0.1)	51.9(2.9)	26.8(2.3)	10.7(1.6)	10.6(1.8)
60	0.7(0.1)	52.6(2.9)	22.1(1.8)	12.1(1.7)	13.2(2.4)
Thermally modified dark alder					
Ref.	0.26(0.04)	65.7(3.1)	21.5(3)	7.2(1)	5.6(0.8)
5	0.68(0.03)	29.5(3.1)	27.4(2)	16.7(1.6)	16.5(1.7)
10	0.65(0.04)	32.2(2.4)	31.5(2)	14.9(1.9)	21.5(1.9)
60	0.78(0.08)	40.3(2.9)	33.9(2.2)	13.1(1.7)	12.6(1.8)
Thermally modified ash					
Ref,	0.28(0.09)	70(5)	19.6(4.7)	6.5(1.7)	3.85(2)
5	0.56(0.05)				
10	0.59(0.07)				
60	0.71(0.08)	40.1(2.2)	31.1(1.9)	14(2)	14.7(1.9)
Thermally modified aspen					
Ref,	0.32(0.08)	58.3(2.8)	29.6(1.6)	8(1)	4.1(1)
5	0.59(0.07)	23.4(2.2)	32.1 (2.8)	23.1(3.2)	21.4(4.1)
10	0.69(0.09)	21()	39.8()	16.4()	23.3()
60	0.83(0.09)	31.5(5)	38.3(4.8)	15.1(2.1)	15(1.9)
Thermally modified radiata pine					
Ref.	0.26(0.08)	64.7(4.6)	25.1(4)	5.8(1)	4.5(0.9)
5	0.52(0.05)	45.2(2.3)	26.4(5.2)	13.2(2.5)	15.3(4.5)
10	0.53(0.05)	31.2()	26.3()	20.4()	22.2()
60	0.77(0.06)	52(5.1)	28.9(4.6)	9.4(1.8)	9.6(2.6)

The clear increase of C2, C3 and C4 components was observed for all species already after 5 s of plasma treatment but as the treatment time was increased no obvious trends could be observed and the at% of these components varied from species to species. It should be noted however that charging problems were encountered also with other species thus the fits of the C1s band were not always ideal resulting in larger uncertainty of the C1s components.

Correlation between surface free energy and the O/C ratio

The observed similar asymptotic increase of the O/C ratio and surface free energy with plasma treatment time suggests a correlation between the two quantities. Figure 5 displays the correlation between surface free energy and O/C ratio for the investigated thermally modified wood species after plasma treatment. A linear fit ($R^2 > 0,88$) was found to be suitable for all species. Similar linear correlation was found to characterize the dependence between the wetting parameters of water advancing contact angles on the O/C ratio after thermal treatment at varying temperatures of Cathay poplar and Scots pine [9]. An increased thermal treatment temperature resulted in reduced O/C ratio and reduced wetting of the thermally treated wood surface. In the present work, the plasma treatment increased the O/C ratio which resulted in linear increase of surface free energy and increased wetting with distilled water. This indicates that O/C ratio on the wood surface determines not only the wetting behavior of polar liquids but also the surface free energy provided that the morphology has not changed on the micrometer scale.



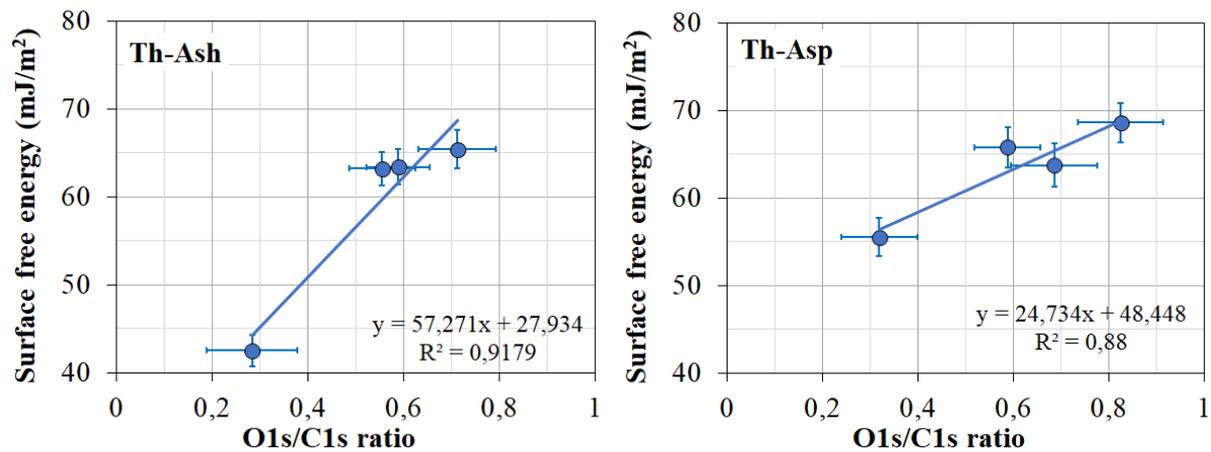


Figure 5. Correlation between SFE and O/C ratio for thermally modified alder, dark alder, ash and aspen after DCSBD plasma treatment. The uncertainty is given as standard deviation.

A reasonably good linear fit ($R^2 > 0.87$ except for thermal aspen with $R^2 = 0.73$) was also found for the polar component of surface energy and the O/C ratio (data not shown). This confirms that the main changes to the surface free energy resulted from the increased polar part due increased O/C ratio.

SEM imaging

Figure 6 shows SEM images of thermal aspen after plasma treatment of 5 s and 60 s. Images taken after 5 s of plasma treatment are identical to the images taken of reference samples without any plasma treatment (not shown). On the micrometer scale increasing the plasma treatment time up to 60 s did not change the surface morphology (figure 6 a and b). However, high magnification images taken after 60 s of plasma treatment reveal structures with dimensions under a few hundred nanometers (Fig. 6 d). Similar structures were observed for thermally modified dark alder, aspen and ash (both on early and latewood).

Recently, plasma structuring effect was observed on beech wood treated with atmospheric pressure plasma jet with a similar treatment time of 60 s at a distance of 10 mm [35]. However, in that work the DCSBD plasma treatment at a distance of 0 mm did not result in the formation of such structuring effect. In this work we observed these structures (Fig. 6d) to be sensitive to certain parameters such as treatment time and distance from the DCSBD surface. It is also possible that in case of DCSBD the wood surface structuring occurs with thermally modified wood. Further studies are needed to determine the exact dependence on the said parameters.

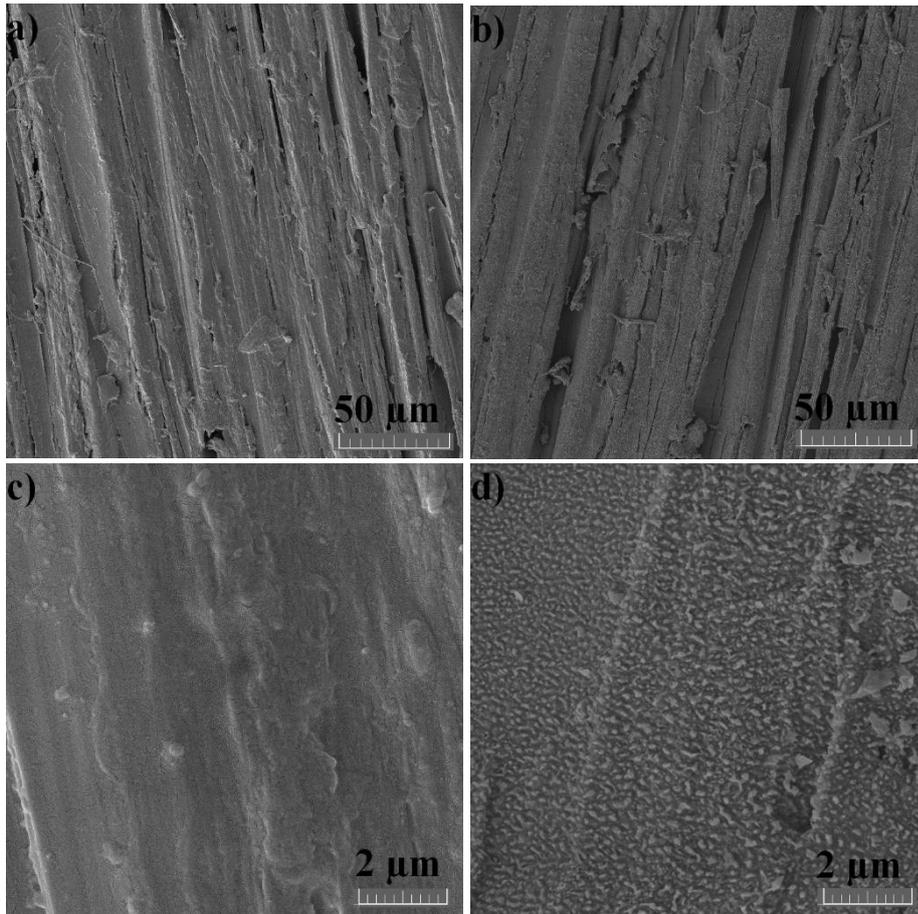


Figure 6. SEM images of thermally modified aspen after 5 s of plasma treatment (a and c) and 60 s of plasma treatment (b and d).

It is known that lignin is more resistant to plasma etching than other wood constituents [36]. One possible explanation for the creation of these structures is that plasma facilitated a partial etching of the wood surface, which revealed lignin e.g. in the middle lamellae where it has a relatively high concentration [37]. This assumption is supported by the increase of the C1 peak assigned to lignin when the plasma treatment time was increased from 10 to 60 s. However, the validation of the constituents and cause of these structures requires further studies.

The SEM images presented in [21] revealed only minor defects on the surface caused by etching with comparable treatment times as in this study. However, in that study the plasma energy density was substantially lower. It should also be pointed out that the appearance of these structures after 60 s of DCSBD treatment does not affect the correlation between the surface free energy and O/C ratio which lies well on the linear fit. Therefore, it can be concluded that the main cause of increased surface energy with plasma treatment time is due to the changes in the surface chemistry i.e. the increased O/C ratio and not the nanoscale induced changes on the surface at longer treatment times.

Summary

DCSBD plasma with varying treatment time was applied to thermally modified wood species.

The wood surface was characterized with contact angle measurements, XPS and SEM.

The reference values of surface free energy varied with wood species but after 5 and 10 s of plasma treatment a similar value of 63- 64 mJ/m² was observed for all species except thermally modified radiata pine which had a surface energy too high to measure with this method. XPS measurements showed an increased O/C ratio after plasma treatment. A linear correlation was found between the surface free energy and O/C ratio.

SEM imaging revealed that after plasma treatment the thermally modified surface structure is unchanged on the micrometer scale. Longer DCSBD treatment times of 60 s revealed nano-scale structures. These surface structures could have a different effect on the surface properties depending on the investigated species. This however requires further studies.

Acknowledgments

This work was supported by the Estonian Research Council (grant No. PUTJD732) and project LO1411 (NPU I) funded by Ministry of Education, Youth and Sports of Czech Republic.

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