PLASMA SURFACE TECHNOLOGY PROMOTING CAPILLARY IMPREGNATION OF WOOD: XPS ANALYSIS OF DIFFERENT PLASMA PRE-TREATED WOOD SURFACES

Assist. Prof. Ivanov I. [1], Assoc. Prof. Gospodinova D. Ph.D. [1], Prof. Dineff P. Ph.D. [1], Prof. Veleva L. Ph.D. [2]
Faculty of Electrical Engineering - Technical University of Sofia, Bulgaria [1]
CINVESTAV - Merida, Yucatan, Mexico [2]
E-mail: dilianang@abv.bg

Abstract: *X-ray Photoelectron Spectroscopy (XPS) also referred to as Electron Spectroscopy for chemical analysis (ESCA) was used to characterize the surfaces of plasma-chemical treated wood in air by dielectric barrier discharge (DBD). The plasma-surface pre-treatment of wood, wooden products and cellulosic fibrous materials has been developed for promoting capillary impregnation and plasma-aided flame retardency. In this study, XPS has been used since it has proved to be suitable investigation method to characterize the composition of a plasma pre-treated material surface. This method is a powerful analytical and non-destructive technique which has already been used for the analysis of plasma modified wood surfaces and in the characterization of wood's reactions. Changes due to the plasma-chemical process were identified from the survey large spectra as well as from the detailed C_{1s} and O_{1s} spectra. The oxidative changes were quantified with the atomic ratio of oxygen to carbon and with a detailed analysis of the contributions to the C_{1s} and O_{1s} peaks.*

Keywords: ATMOSPHERIC DIELECTRIC BARRIER DISCHARGE (*DBD*), FLAME RETARDANT, CAPILLARY IMPREGNATION, TROPICAL (RAIN-FOREST) WOOD, X-RAY PHOTOELECTRON SPECTROSCOPY (*XPS*).

1. Introduction

The plasma aided flame retardation of wood and wood products has been developed as a result of a new plasma-aided process of *capillary impregnation* that comprises a surface plasma pre-treatment for alteration of the chemical, electrical (ionic), and capillary activities of wood surface, in general for improvement the technological characteristics of the capillary impregnation process. This study has been developed as part of a large research on plasma-chemically activated wood surface and flame retardant treated rain-forest wood.

A technological system of air plasma device and applicators has been created to produce cold technological plasma through dielectric barrier discharge (*DBD*) at atmospheric pressure and room temperature. The cold plasma pre-treatment by non-equilibrium *DBD* of wood, like rain-forest woods - *Tzalam*, *Caoba Mahogany*, and *Mexican White Cedar* (Mexico, Yucatán), improves technological characteristics such as solution spreading and wicking speed, as well as specific amount of the sorbed flame retardant. Due to its fine-texture and surface inactivation it is difficult to apply flame retardants directly through capillary impregnation. In this way, the plasma pre-treatment of wood and wooden products improves its flame retardation. The plasma-chemical surface pre-treatment by dielectric barrier air discharge at atmospheric pressure (*DBD*) was specified as a new good way for wood surface functionalization and activation [1, 2, 3, and 4].

Wood is a complex material constituted mainly of three biopolymers: lignin, cellulose and hemicelluloses. In addition to these polymeric components, wood may contain extractives in more or less large quantities including several classes of organic compounds like sugars, flavonoids, tannins, terpenes, fats or waxes. Well-suited for the study of surface chemistry of complex organic materials, *X-ray photoelectron spectroscopy* (*XPS*) also referred to as *Electron Spectroscopy for chemical analysis* (*ESCA*) has been widely used in order to investigate the surface chemical composition of numerous lignocellulosic materials especially in the field of pulp and paper, where the surface chemistry is of considerable importance for the properties of the final products. Similarly, some reported studies investigate the changes of surface chemistry after different wood transformation processes and processing [4 and 5].

X-ray photoelectron spectroscopy is a surface chemical analysis technique that can be used successfully to analyze the surface chemistry of a material in its "*as received*" state, or after some treatment such as plasma-chemical surface pre-treatment. The binding energy is a characteristic of the atoms, which can be used for elemental identification on the plasma chemically modified wood surface.

The interpretation of the curve fit of the carbon C 1s peak after *Kazayawoko* (1998) was used to interpret the changes of wood surface chemistry after plasma *DBD* pre-treatment. To obtain a deeper insight into the various functional groups, the C 1s signal is usually deconvoluted into four components according to the number of oxygen atoms bonded to *C*, [5]:

□ The C_1 class corresponds to carbon atoms bonded only with carbon or hydrogen atoms (C-C or C-H), and it is usually pointed out at a *binding energy* (*BE*) of 284.6 eV (some also use 285.0 eV as the nominal value for the binding energy of carbon);

□ The C_2 class reveals the carbon atoms bonded with one oxygen atom (C-O or C-OH), and it appears at a higher binding energy compared to C_1 (Δ_{BE} = + 1.5 ± 0.2 eV) - 286.1 ± 0.2;

□ The C_3 class corresponds to carbon atoms bonded to a carbonyl (C=O) or two non-carbonyl oxygen atoms (O-C-O), and it appears at a higher binding energy compared to C_1 (Δ_{BE} = + 2.8 ± 0.2 eV) - 287.4 ± 0.2 .

□ And finally, the C_4 class is associated with carbon atoms bonded to a carbonyl and a non-carbonyl oxygen atom (O-C=O) - it appears at a higher binding energy compared to C_1 (Δ_{BE} = + 3.75 ± 0.2 eV) - 288.35 ± 0.2.

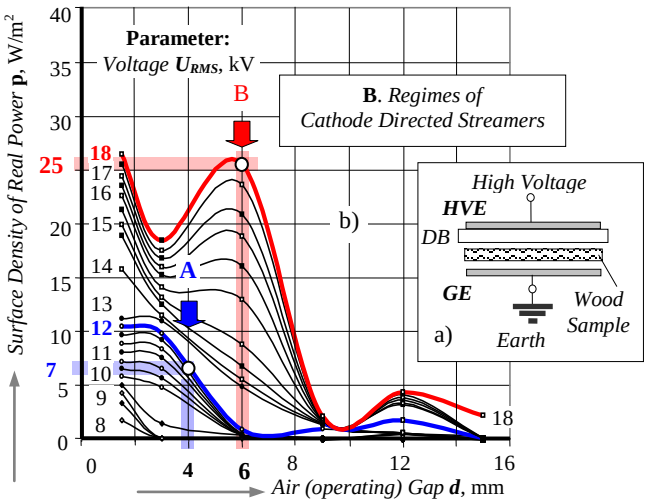

Fig. 1. Plasma-chemical surface pre-treatment of wood sample by non-equilibrium dielectric barrier air discharge at atmospheric pressure in asymmetric coplanar system with one glass barrier (**a**), technological regimes (*A* and *B*) of cathode directed streamers (**b**).

Table 1: Elemental surface composition of three heartwood species before (*K*) and 2 hours after plasma pre-treatment (*DBD*: 12/18 kV) determined from wide *XPS*-spectra.

Wood	*Samples*	*Peaks on the Wide XPS-spectra - Chemical Surface Composition*, at. %						
	Peaks	**C**	**O**	**N**	**P**	**Si**	**nO/nC**
Tzalam Heartwood	*K* (Non-Treated)	**83.71**	**14.49**	1.53	-	0.27	**0.17**
	DBD Pre-treated	12 kV (50 Hz)	66.55	32.43	1.03	-	-	0.49
		18 kV (50 Hz)	61.38	37.63	0.99	-	-	0.61
Caoba Mahogany Heartwood	*K* (Non-Treated)	**81.12**	**18.39**	0.49	-	-	**0.23**
	DBD Pre-treated	12 kV (50 Hz)	78.25	20.17	1.58	-	-	0.26
		18 kV (50 Hz)	71.06	28.21	0.73	-	-	0.40
Mexican White Cedar Heartwood	*K* (Non-Treated)	**79.86**	**17.75**	1.41	-	0.98	**0.22**
	DBD Pre-treated	12 kV (50 Hz)	61.34	35.17	1.44	2.05	-	0.57
		18 kV (50 Hz)	66.83	29.92	2.24	1.01	-	0.45

This is a necessary condition to get better knowledge of the chemical transformations occurring during plasma-chemical surface pre-treatment and to propose an interpretation in terms of existing and known mechanisms.

The objective of this paper was to study the effect of plasma chemical surface pre-treatment of *DBD* in air (oxidative atmosphere) at atmospheric pressure and room temperature at industrial frequency (50 Hz) and two voltages - 12 and 18 kV (RMS), on the wood surface functionalization monitored by surface chemical composition change. Therefore, we focused mainly on the O/C ratio evolution and on the changes in the various components of the C (1s) and O (1s) lines.

2. Experimental Investigation

On basis of prior art, as well as on our own experience in plasma-aided impregnation of wood and wooden materials, [1, 2], an oxidative surface plasma pre-treatment has been applied on the test samples for 60 sec in a non-equilibrium cold plasma of *DBD* at atmospheric pressure. Similar changes are the basis of the expected *DBD*-surface functionalization effect on the three species of rain-forest wood samples, plasma pre-treatment in two types of *DBD* in air was performed: *i*) *A - DBD* at industrial frequency (50 Hz) and relatively low voltage (12 kV RMS; 16.9 kV PV) at which the discharge regime is transitionally from electron avalanche to cathode directed streamers; *ii*) *B - DBD* at industrial frequency and relatively high voltage (18 kV RMS; 25.4 kV *PV*) characterizing the regime of cathode directed streamers, Fig. 1.

X-ray photoelectron spectroscopy analysis was carried out by using a photoelectron spectrometer *VGS ESCALAB Mk II* with monochromatic *AlKα* radiation source (*FWHM* = 0.5 eV). *XPS-spectra* were obtained by irradiating a wood sample with a beam of *X-rays*. The angle between the directions of the incident *X-ray* and that of the observations (fixed by analyzer entrance slit) was 50.

Studies of *cold plasma functionalization phenomena on wood*, i.e. interactions of oxidative cold plasma with wood surface, may add valuable information about the capillary impregnation, gluing and coating properties of wood. Such information is essential in the development of efficient processing methods, and for the prediction of the functionality and durability of wood products.

Three species of Mexican rain-forest heartwood were investigated: *i - Tzalam* (*Lysiloma bahamensis*); *ii - Caoba Mahogany* (*Swietenia macrophylla*); and *White Cedar* (*Cupressus Lusitanica*).

3. Results and Discussion

The results from the wide *XPS* survey spectra of investigated wood samples before (*DBD* non-treated) and two hours after plasma chemical treatment (*DBD* pre-treated) are presented in Table 1. Analysis of the survey spectra indicates the presence of carbon (*C*), oxygen (*O*) and small amounts of nitrogen (*N*), phosphor (*P*) and silicon (*Si*) which represent the expected elements in wood.

High-resolution scans of the *XPS* spectra of C (1s) and O (1s) levels are also presented with their decomposition into components, respectively Fig. 2 and 3.

Using the total areas of these peaks and the respective photoemission cross-sections, a quantitative determination of the O/C ratio can be calculated. By knowing the chemical composition of each of these components, it is possible to calculate *a priori* the theoretical O/C ratio characteristic of non-treated wood samples [5].

Table 2. *Carbon peak C (1s) components or proportions of oxygen (O) and carbon (C) functional groups of heartwood surfaces before (K) and 2 hours after plasma surface pre-treatment (DBD:*12/18 kV*) determined from high-resolution XPS-spectra.*

Woods	*Samples*		*Carbon peak C_{s1} components*, area %								
			C1 (C-C or C-H)	**C2** (C-O or C-OH)	**C2-3** (ND)	**C3** (C=O or O-C-O)	**C4** (O-C=O)	**C4-** (ND)	nC1/ nC2	**Sum** (nC2+ nC3	nC2/ (nC2+nC3)
			(**285.0** ±0.4 eV)	(**286.0** ±0.4 eV)	(287.0 ±0.4 eV)	(**288.7** ±0.4 eV)	(**289.5** ±0.4 eV)	(292.8 ±0.4 eV	-	-	-
Tzalam Heartwood	*K* (Untreated)		56.79	**15.20**	0.00	**4.14**	0.00	0.00	**5.31**	**19.34**	**0.79**
	DBD Pre-treated	12 kV	35.04	27.12	22.01	15.27	0.00	0.56	1.29	42.39	0.64
		18 kV	42.33	30.92	15.35	9.23	0.00	2.17	1.40	40.15	0.77
Caoba Mahogany Heartwood	*K* (Untreated)		57.22	**12.67**	0.00	**6.23**	0.00	0.00	**6.40**	**18.90**	**0.67**
	DBD Pre-treated	12 kV	49.65	26.14	0.00	14.71	9.50	0.00	1.90	40.85	0.64
		18 kV	51.69	22.92	0.00	12.29	13.10	0.00	2.26	35.12	0.65
Mexican White Cedar Heartwood	*K* (Untreated)		54.22	**17.40**	0.00	**4.60**	0.00	0.00	**4.48**	**22.00**	**0.79**
	DBD Pre-treated	12 kV	45.94	27.96	15.05	5.98	0.00	5.07	1.64	33.94	0.82
		18 kV	50.23	20.74	15.22	13.10	0.00	0,71	2.42	33.84	0.61

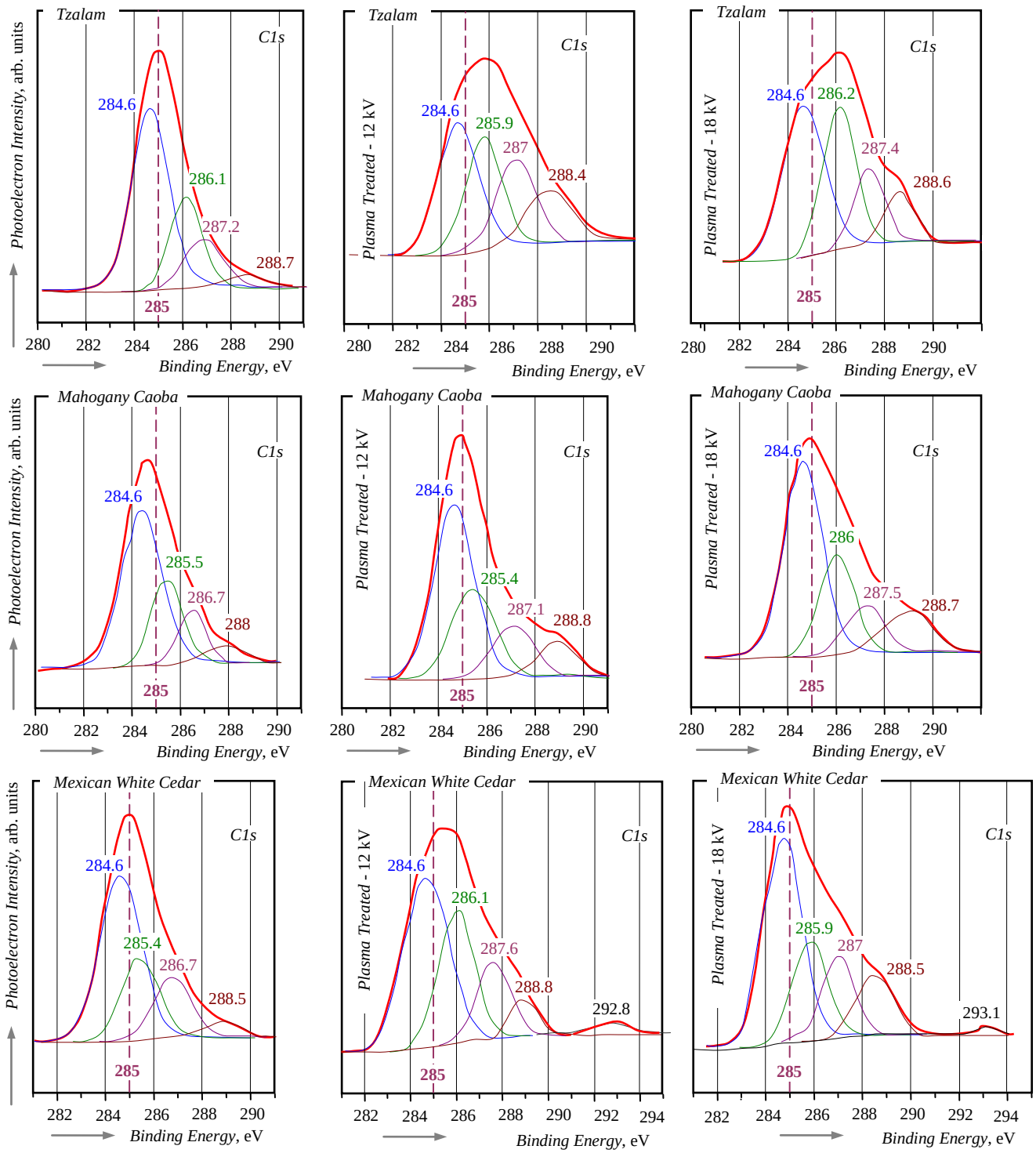

Fig. 2. Carbon *C (1s)* peak in photoelectron *XPS/ESCA* spectra of bare samples of heartwood and 2 hours after plasma surface pre-treatment in atmospheric dielectric barrier discharge in air at industrial frequency (50 Hz) and 12 and 18 kV (RMS) voltage.

Cellulose comprises five carbon atoms of C_2 and one of C_3 with an O/C of **0.83**. *Hemicelluloses*, which are mainly represented by glucuronoxylans, are constituted of fewer than five carbon atoms of C_2, less than one carbon atom of C_4 for the acetyl and carboxylic groups and one atom of C_3 with an O/C of approximately **0.8**0. The contribution of *lignin* is more complex and therefore more difficult to quantify. Four types of carbons are present in its structure with a greater contribution from the C_1 and C_2 classes and an O/C ratio of roughly **0.33.** *Extractives* are also present in very small quantities in wood and their contribution to the overall *XPS* spectrum is relatively low - for example carbon atoms of C_4 class are present in *linolic* and *abietic* acid with an O/C of 0.11/0.10, respectively [**5]**.

From the data of untreated wood samples, it appears that carbon atoms bonded with one oxygen atom (C_2 class) are the most abundant. Carbon atoms bonded with other carbon or hydrogen (C_1 class) or bonded with two oxygen atoms (C_3 class) are present in smaller proportions, while those bonded with three oxygen atoms are less abundant Table 2.

The O/C ratio may be estimated from the individual ratio and abundance of each component, or from the elemental composition determined experimentally in the case of untreated wood samples. According to these methods, the O/C ratios are found to be of and 0.17, 0.22 and 0.23, respectively,Table 1.

The O/C ratio and distribution of carbon atoms of plasma treated samples differ considerably from those obtained for untreated wood: 0.49, 0.26 and 0.57 (*DBD*:12 kV); 0.61, 0.40 and 0.45 (*DBD*: 18 kV). The increased O/C ratio is attributed to the important oxidation occurring during cold plasma-treatment: the C_1 (C-C; C-H) contribution decreased considerably while

Table 3. *Oxygen peak O (1s) components or proportions of oxygen (O), carbon (C) and hydrogen (H) functional groups of heartwood surfaces before (Tzalam-K) and after plasma surface pre-treatment (DBD*: 12/18 kV*) determined from high-resolution XPS-spectra.*

Woods	*Samples*	**O1** (O=C)	**O2** (O-H)	**O3** (O-C; H-O-H)	Sum1 (O_1;O_3)	Sum2 (C_2;C_3)	Sum1 (O_1;O_3) - Sum2 (C_2;C_3) (H-O-H)	**$O3^1$** (O-C)
	Binding energy, eV	**531.5**±0,4	**532.5**±0,4	**533.0**±0,4				
Tzalam (*Lysiloma bahamensis*)	*K*: untreated	0.00	**58.48**	**41.51**	41.51	19.34	**22.17**	**19.34**
	DBD: 12 kV (50 Hz)	0.00	56.21	43.79	43.79	42.39	1.40	42.39
	DBD: 18 kV (50 Hz)	0.00	58.74	41.26	41.26	40.15	1.11	40.15
Caoba Mahogany (*Swietenia macrophylla*)	*K*: untreated	0.00	**58.00**	**42.00**	42.00	18.90	**23.10**	**18.90**
	DBD: 12 kV (50 Hz)	0.00	58.62	41.38	41.38	40.85	0.53	40.85
	DBD: 18 kV (50 Hz)	0.00	56.72	43.28	43.28	35.12	8.16	35.12
Mexican White Cedar (*Cupressus Lusitanica*)	*K*: untreated	0.00	**53.22**	**46.78**	46.78	22.00	**24.78**	**22.00**
	DBD: 12 kV (50 Hz)	0.00	61.43	38.57	38.57	33.94	4.63	33.94
	DBD: 18 kV (50 Hz)	0.00	56.70	43.30	43.30	33.84	9.46	33.84

the C_2 (C-O; C-OH), C_3 (C=O; O-C-O) contribution increased, and C_4 (O=C-O) appears in *Caoba Mahogany*, indicating that the content of C-O, C-OH, C=O, O-C-O and O=C-O groups becomes more important. This plasma modification can not be attributed to an increase of the lignin content due to preferential degradation of hemicellulose.

Figures 2 and 3 show typical *XPS* survey spectra and high resolution C (1s) and O 1s spectra of plasma-treated Tzalam, Caoba mahogany and White cedar wood. When comparing C 1s spectra presented in Fig. 2, it is clear that the contribution of the different types of carbons differs strongly between untreated and plasma-treated wood samples. C_3 and C_2 contributions increased highly, while the C_1 contribution (attributed to lignin) decreased seriously after plasma-treatment.

The contribution of the different types of oxygen atoms is much more difficult to analyze, Fig. 3. O_1 and O_3 classes report the contribution of two types of carbon atoms - O=C and O-C while C_2 and C_3 classes report the contribution similarly of different types of oxygen atoms - C-O, C-OH, C=O and O-C-O. The difference between *Sum1* (O_1 + O_3) and *Sum2* (C_2 + C_3) can be attributed to the amount of water on the wood surface (H-O-H), Table 3.

The plasma chemical surface modification removes successfully the water (H-O-H) from the wood surfaces. The difference (*Sum1-Sum2*) was decreased highly two hours after plasma pre-treatment: *Tzalam* - form 22.17 to 1.40/1.11; *Caoba Mahogany* - from 23.10 to 0.53/8.16; and *Mexican white cedar* - from 24.78 to 4.63/9.46, respectively, Table 3.

The O_3 class reveals the oxygen atoms bonded with one carbon atom and two hydrogen atoms (O-C and H-O-H). A new difference between O_3 class and the difference (*Sum1-Sum2*) reveals the abundance of oxygen atoms bonded with other carbon atom (O-C). From the data of untreated and plasma treated wood samples, it appears that carbon atoms bonded with one oxygen atom (C_2 or O_3[1] class) increase essentially its quantity after plasma treatment: *Tzalam* - form 19.34 to 42.39/40.15; *Caoba Mahogany* - from 18.90 to 40.85/35.12; and *Mexican white cedar* - from 22.00 to 33.94/33.84, respectively, Table 3.

When using high energy resolution experiment settings on *XPS* equipped with a monochromatic Al K-alpha X-ray source, the *Full Width at Half Maximum* (*FWHM*) of the main investigated *XPS*-peaks range from:

□ The C_1, C_2, C_3 and C_4, or C (1s) component, peaks of untreated (bare) woods have *FWHM*s that, in general, range from 1.3 eV to 2.0 eV: *Tzalam* - from 1.6 to 2.0; *Caoba Mahogany* - from 1.3 to 2.0; and *Mexican white cedar* - from 1.8 to 2.0;

□ The C_1, C_2, C_3 and C_4 peaks of plasma treated (*DBD*: 12 kV) woods have *FWHM*s that, in general, range from 1.4 eV to 2.34 eV: *Tzalam* - from 1.8 to 2.2; *Caoba Mahogany* - from 1.98 to 2.16; and *Mexican white cedar* - from 1.4 to 2.34.

□ The C_1, C_2, C_3 and C_4 peaks of plasma treated (*DBD*: 18 kV) woods have *FWHM*s that, in general, range from 1.4 eV to 2.34 eV: *Tzalam* - from 1.42 to 2.1; *Caoba Mahogany* - from 1.75 to 2.38; and *Mexican white cedar* - from 1.0 to 1.91.

□ The O_1, O_2, and O_3, or O (1s) component, peaks of untreated woods have *FWHM*s that, in general, range from 1.8 eV to 2.44 eV: *Tzalam* - 2.38; *Caoba Mahogany* - from 1.97 to 2.44; and *Mexican white cedar* - from 1.8 to 2.0;

□ The O_1, O_2, and O_3, or O (1s) component, peaks of plasma treated (*DBD*: 12 kV) woods have *FWHM*s that, in general, range from 2.24 eV to 2.67 eV: *Tzalam* - from 2.45 to 2.67; *Caoba Mahogany* - from 2.40 to 2.63; and *Mexican white cedar* - from 2.24 to 2.25;

□ The O_1, O_2, and O_3, or O (1s) component, peaks of plasma treated (*DBD*: 18 kV) woods have *FWHM*s that, in general, range from 1.3 eV to 2.0 eV: *Tzalam* - from 2.17 to 2.37; *Caoba Mahogany* - from 2.53 to 2.57; and *Mexican white cedar* - from 2.3 to 2.58;

Conclusion

Processes of woods preservation and bonding are usually achieved through the application of impregnation solution or adhesive on wood surface. Among the different mechanisms involved in the impregnation and bonding of woods, two synergistic effects seem essential in order to achieve good results:

□ The penetration and anchoring of the impregnation solution or adhesive in the void spaces of the wood surface;

□ The occurrence of a strong interaction or chemical reaction between the impregnate or adhesive and the major constituents of wood.

These conditions are governed by the surface properties that depend not only on the bulk composition, but also on the surface building and modification process.

X-ray photoelectron spectroscopy is a suitable investigation method to characterize the composition of wood surface. *XPS* is the most widely used surface analysis technique because of its relative simplicity in use and data interpretation. It was used successively to investigate the interaction of three rain-forest wood surfaces with cold non-equilibrium plasma of *DBD* in air at atmospheric pressure and room temperature.

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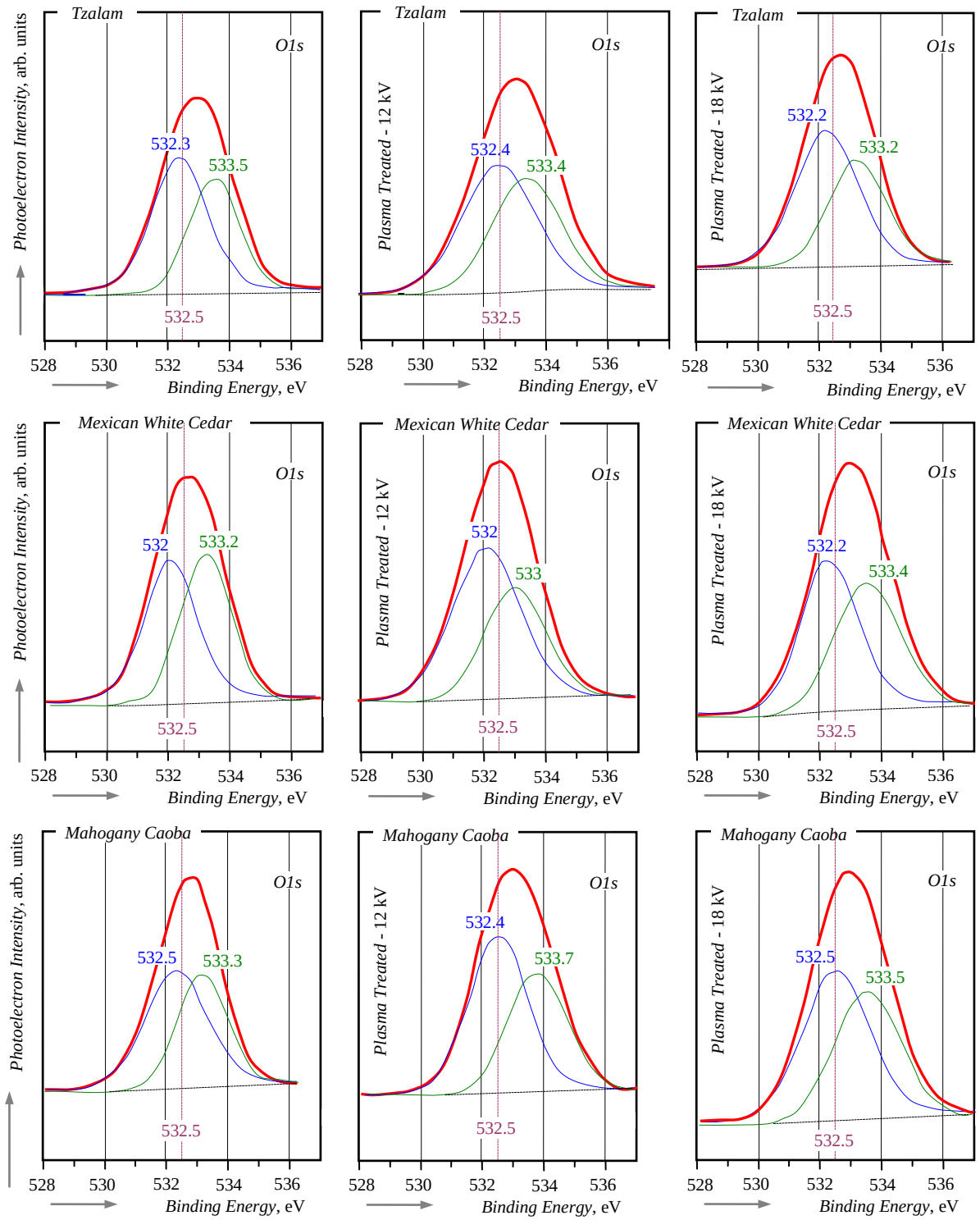

Fig. 3. Oxygen *O1s* peak in photoelectron *XPS/ESCA* spectra of bare sample of heartwood and 2 hours after plasma surface pre-treatment in atmospheric dielectric barrier air discharge at industrial frequency (50 Hz) and 12 and 18 kV (RMS) voltage.

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