INVESTIGATION ON PLASMA AIDED FLAME RETARDATION OF TZALAM WOOD (*LYSILOMA BAHAMENSIS*) BY XPS-ANALYSIS

Assoc. Prof. M.Sc. Gospodinova D. Ph.D. [1], M.Sc. Ivanov I. [1], Prof. M.Sc. Dineff P. Ph.D. [1], Prof. M.Sc. Veleva L. Ph.D. [2]
Faculty of Electrical Engineering - Technical University of Sofia, Bulgaria [1]
CINVESTAV - Merida, Ycatan, Mexico [2]

dilianang@abv.bg

Abstract: *The plasma aided flame retardation of wood, wooden products and cellulosic fibrous materials has been conceived and developed as a result of a plasma aided process of capillary impregnation. The dielectric barrier discharge surface pre-treatment modifies the chemical activity of wood and improves such characteristics of the impregnation process as the penetration depth, speed of solution spreading and adsorption, and capacity of adsorbed solution. The effect of plasma-aided capillary impregnation with phosphor and nitrogen containing flame retardants onto the wood surface functionalization was investigated and monitored on Tzalam wood (Yucatan, Mexico) by X-ray photoelectron spectroscopy (XPS-analysis, ESCA).*

Keywords: DIELECTRIC BARRIER DISCHARGE PRE-TREATMENT, FLAME RETARDATION OF CELLULOSIC FIBROUS MATERIALS, PLASMA AIDED CAPILLARY IMPREGNATION, X-RAY PHOTOELECTRON SPECTROSCOPY

1. Introduction

Wood and wooden products/materials are thermally degradable and combustible materials. Wood products can contribute to unwanted fires and be destroyed as well. Minor amounts of thermal degradation adversely affect structural properties. Therefore, knowledge of the thermal degradation and fire performance of wood can be critical in many applications, [1].

Chemical surface treatments of wood or its flame retardation are available to improve wooden fire performance characteristics. Flame-retardant treatments in general reduce the initial peak heat release, average heat release, and the effective heat of combustion. Ignition times are often increased successfully. Excessive levels of flame-retardant treatment can increase the production of smoke. Flame-retardant treatments tend to have minimal impact on charring rates and the fire endurance of structural members, [1].

For interior applications where leaching is not an issue, water-soluble nitrogen and phosphor inorganic salts containing are the common flame retardants. These salts include monoammonium and diammonium phosphate, ammonium sulfate, zinc chloride, sodium tetraborate, and boric acid. These chemicals are combined in water solution formulations to develop optimum fire performance (flaming, smoldering, and smoke production) yet still retain acceptable hygroscopicity, strength, corrosivity, and other properties, [2, 3].

The plasma-aided flame-retardation treatment of wood and wooden products has been developed as a result of a new plasma-aided process of capillary impregnation with new water soluble nitrogen and phosphor containing salts. The plasma-chemical surface pre-treatment increases the chemical activity of wood surface as well as its electrical (or ionic) and capillary activities, and in general improves the technological characteristics of the capillary impregnation process.

The cold plasma pre-treatment by non-equilibrium dielectric barrier discharge (*DBD*) at atmospheric pressure and room temperature improves technological capillary impregnation (spreading, brushing, and rolling) characteristics such as the solution spreading and the adsorption speed, as well as the specific amount of the adsorbed flame retardant inorganic water solution. In this way, the plasma pre-treatment of wood and wooden products/materials improves its flame retardation [2, 3].

Tzalam wood is well known largely used in non-structural constructions, flooring and panelling. This wood is highly durable and easy to work, finishes smoothly and takes a fairly high natural polish. But due to hardwoods relatively high density, fine-texture and surface inactivation it is difficult to apply this kind of flame retardants through capillary impregnation. The plasma-chemical surface pre-treatment by dielectric barrier air discharge at atmospheric pressure (DBAD) was specify as new good way to *Tzalam* wood surface functionalization and activation [5].

The objective of this paper was to study the effect of plasma-aided flame-retardant capillary impregnation by the wood surface functionalization. *X-ray photoelectron spectroscopy* (*XPS*) or *electron spectroscopy for chemical analysis* (ESCA) was used as a very powerful non-destructive surface chemical analysis technique which provides valuable data on chemical surface composition and surface reorganization after plasma-aided chemical treatment. The binding energy is a characteristic of the atoms, which can be used for elemental identification on the plasma-aided chemically modifying wooden surface. This study was developed as part of a large investigation on plasma-chemically activated and flame retarded wood surface [2, 3, and 5].

2. Experimental Investigation

Subject of this research was a flame-retardation treatment after oxidative cold plasma (*DBD*-) pre-treatment in air at atmospheric pressure. It is well known that the surface plasma-chemical modification was accompanied with an accumulation of oxygen containing groups on the surface an effect depending on the operation conditions, [4].

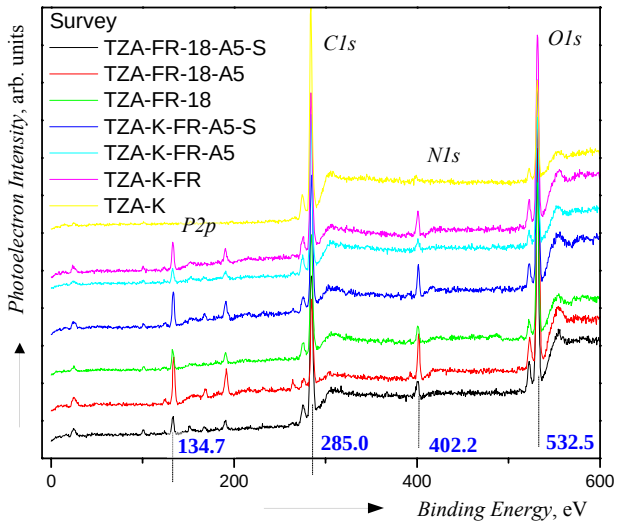

Fig. 1. Wide *XPS/ESCA* spectra of *Tzalam* heart wood surfaces after capillary impregnation with phosphor and nitrogen containing flame retardant solution before (Tza-K-) and after plasma pre-treatment (50 Hz; 18 kV RMS) and capillary impregnation (Tza-FR-18-).

Similar changes were the basis of the expecting *DBD*-surface activation effect on the *Tzalam*-wood surface after plasma pre-treatment in *DBD* in air at atmospheric pressure at industrial

Table 1. *Elemental composition of* ***Tzalam*** *heart wood surfaces after capillary impregnation with phosphor and nitrogen containing flame retardant solution before (Tza-K-) and after plasma pre-treatment (Tza-18-) determined from wide XPS-spectra.*

Samples of Heart Tzalam wood (Lysiloma bahamensis), Yucatan, Mexico	*Peaks on the Wide XPS-spectra - Chemical Surface Composition,* at. %									
	C	O	N	P	Si	S	nO/nC	nN/nC	nP/nC	nP/nN
Tza-K	**83.71**	**14.49**	**1.53**	**0.000**	**0.2739**	**0.000**	**0.1731**	**0.0183**	**0.0000**	**0.0000**
Tza-K-FR	61.15	26.57	5.375	5.368	1.539	0.000	0.4345	0.0879	0.0878	0.9987
Tza-K-FR-A5	69.51	22.76	2.511	3.611	0.831	0.772	0.3274	0.0361	0.0519	1.4381
Tza-K-FR-A5-S	48.21	34.44	6.721	8.046	1.227	1.358	0.7144	0.1394	0.1669	1.1971
Tza-18	**61.38**	**37.63**	**0.9901**	**0.000**	**0.000**	**0.000**	**0.6131**	**0.0161**	**0.0000**	**0.0000**
Tza-18-FR	59.32	30.42	4.241	5.334	0.6811	OK	0.5128	0.0715	0.0899	1.2577
Tza-18-FR-A5	34.82	42.93	9.426	11.260	0.000	1.570	1.2329	0.0271	0.3233	1.1946
Tza-18-FR-A5-S	58.02	32.44	3.576	4.313	1.651	0.000	0.5591	0.0616	0.0743	1.2091

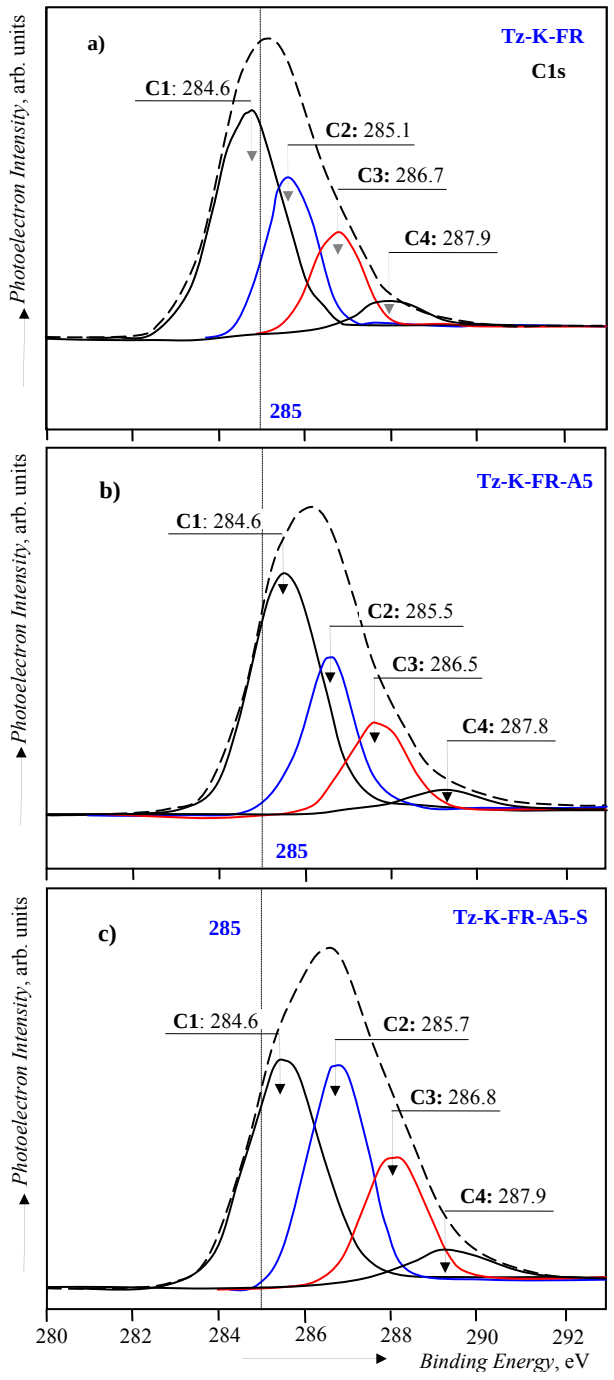

Fig. 2. Carbon *C1s* peak in photoelectron *XPS/ESCA* spectrums after capillary impregnation of bare sample of *Tzalam* heart wood with non-corrected (***a***) and corrected by 5 vol. % anionic surfactant (***b***) or anionic surfactant and 0.1 vol. % spreader (***c***) phosphor and nitrogen containing flame retardant (30 vol. %) impregnating aqueous solution.

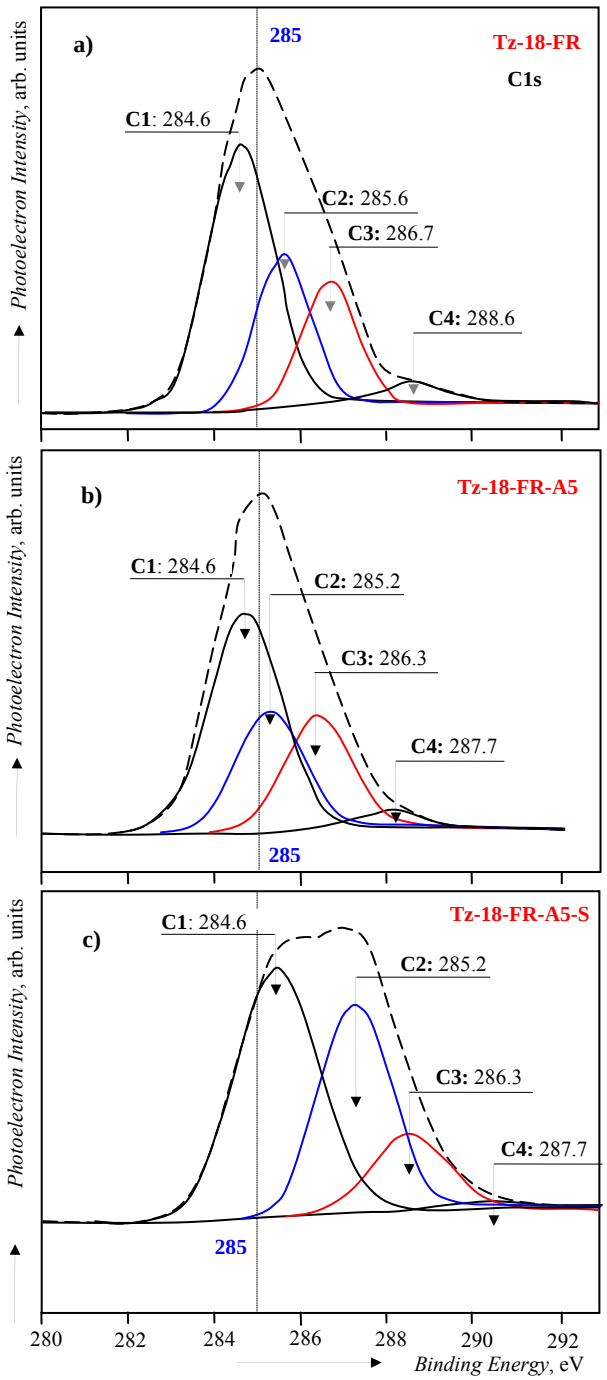

Fig. 3. Carbon *C1s* peak in photoelectron *XPS/ESCA* spectrums after plasma aided capillary impregnation of *Tzalam* heart wood sample with non-corrected (***a***) and corrected by 5 vol. % anionic surfactant (***b***) or anionic surfactant and 0.1 vol. % spreader (***c***) phosphor and nitrogen containing flame retardant (30 vol. %) impregnating aqueous solution.

Table 2. *Carbon peak C_{s1} components or proportions of oxygen (O) and carbon (C) functional groups of Tzalam heart wood surfaces after capillary impregnation with phosphor and nitrogen containing flame retardant solution before (Tza-K-) and after plasma pre-treatment (Tza-18-) determined from high-resolution XPS-spectra.*

Samples	**C1** (C-C or C-H)	**C2** (C-O, C-OH)	**C2-3** (ND)	**C3** (C=O, O-C-O)	**C4** (O-C=O)	**C4-** (ND)	**nC1/ nC2**	**nC1/ nC3**	**Sum (C2;C3)**
Binding energy, eV	**285**±0,4	**286.0**±0,4	**287.2**±0,4	**288.7**±0,4	**289.5**±0,4	**293.0**±0,4	-	-	-
Tza-K	**26862.810**	**11291.190**	**7189.342**	**1959.415**	**0.000**	**0.000**	**2.3779**	**0.0729**	**13250.595**
Tza-K-FR	17614.850	8631.487	5399.564	1732.183	0.000	0.000	2.0408	0.0983	10363.670
Tza-K-FR-A5	17235.870	8618.504	5157.875	1979.824	0.000	0.000	2.0000	0.1149	10350.687
Tza-K-FR-A5-S	11952.180	8494.540	4874.081	1984.022	0.000	0.000	1.4071	0.1660	10478.562
Tza-18	**13139,050**	**9595,501**	**4763,709**	**2864,189**	**0.000**	**673,461**	**1.3693**	**0.2180**	**12459.690**
Tza-18-FR	15335.520	7313.073	5657.962	1139.142	0.000	0.000	2.0008	0.0743	8452.215
Tza-18-FR-A5	8821.104	4408.438	4043.407	716.848	0.000	0.000	2.0040	0.0813	5125.286
Tza-18-FR-A5-S	17408.970	12094.540	4706.130	461.526	0.000	0.000	1.4394	0.0265	12556.066

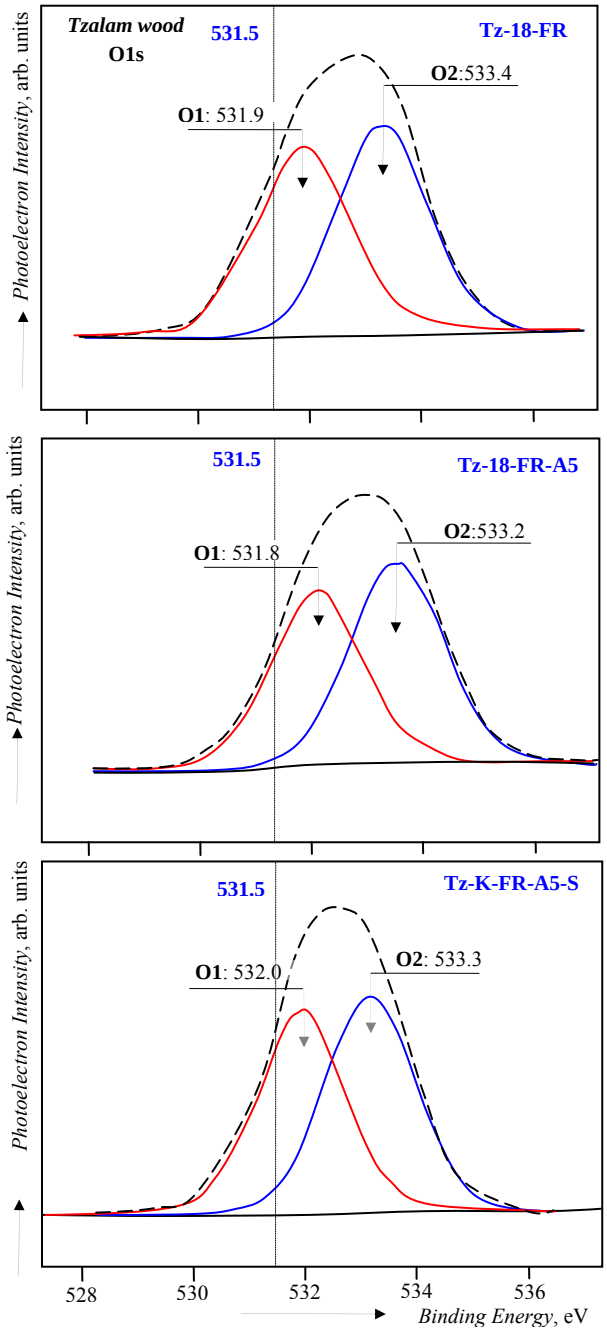

Fig. 4. Oxygen *O1s* peak in photoelectron *XPS/ESCA* spectrums after capillary impregnation of bare sample of *Tzalam* heart wood with non-corrected (***a***) and corrected by 5 vol. % anionic surfactant (***b***) or by anionic surfactant and 0.1 vol. % spreader (***c***) phosphor and nitrogen containing flame retardant (30 vol. %) impregnating aqueous solution.

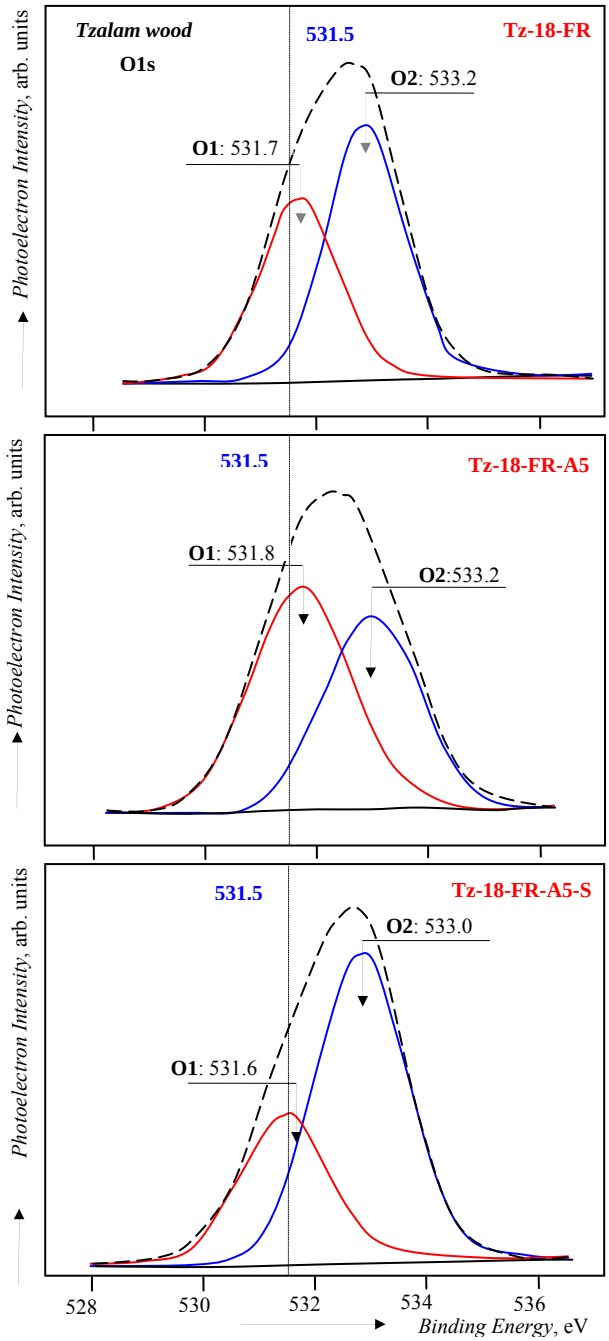

Fig. 5. Oxygen *O1s* peak in photoelectron *XPS/ESCA* spectrums after plasma aided impregnation of *Tzalam* heart wood sample with non-corrected (***a***) and corrected by 5 vol. % anionic surfactant (***b***) or by anionic surfactant and 0.1 vol. % spreader (***c***) phosphor and nitrogen containing flame retardant (30 vol. %) impregnating aqueous solution.

Table 3. *Oxygen peak O_{s1} components or proportions of oxygen (O), carbon (C) and hydrogen (H) functional groups of Tzalam heart wood surfaces after capillary impregnation with phosphor and nitrogen containing flame retardant solution before (Tza-K-) and after plasma pre-treatment (Tza-18-) determined from high-resolution XPS-spectra.*

Samples	**O1** (O=C):	**O2** (O-H):	**O3** (O-C; H-O-H):	**O4** (ND):	**Sum (O1;O3)**	**Sum (C2;C3)**	**Sum (O1;O3) -Sum (C2;C3):** (H-O-H)	**nC1/ nC2**	**nO/ nC**
Binding energy, eV	**531.5**±0,4	**532.5**±0,4	**533.0**±0,4	**534.5**±0,4					
Tza-K	**0.000**	**13775.130**	**9777.978**	**0.000**	**9777.978**	**13250.595**	**-3472.617**	**2.3779**	**0.1731**
Tza-K-FR	22648.850	0.000	22711.430	0.000	45360.280	10363.670	34996.610	2.0408	0.4345
Tza-K-FR-A5	15369.080	0.000	16514.780	0.000	31883.860	10350.687	21533.173	2.0000	0.3274
Tza-K-FR-A5-S	26937.400	0.000	28538.710	0.000	55476.110	10478.562	44997.548	1.4071	0.7144
Tza-18		**30237,730**	**21235,520**	**0.000**	**21235,520**	**12459.690**	**8775.830**	**1.3693**	**0.6131**
Tza-18-FR	17706.910	0.000	24070.290	0.000	41777.200	8452.215	33324.985	2.0008	0.5128
Tza-18-FR-A5	36093.160	0.000	28105.810	0.000	64198.970	5125.286	59073.684	2.0040	1.2329
Tza-18-FR-A5-S	18427.150	0.000	37154.920	0.000	55582.070	12556.066	43026.004	1.4394	0.5591

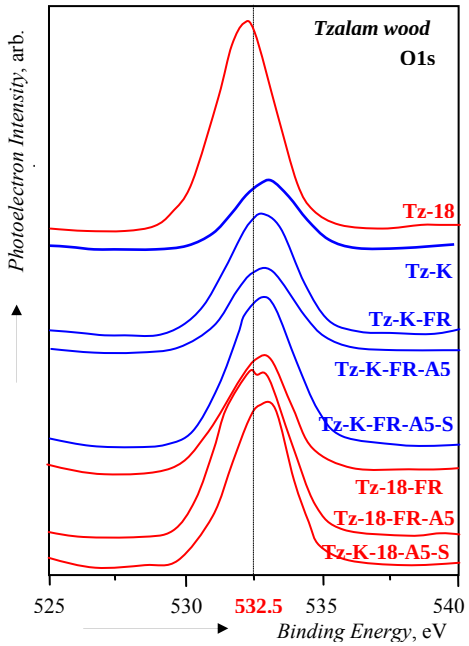

Fig. 6. Oxygen *O1s* peaks in *XPS/ESCA* spectrums of *Tzalam* heart wood samples after non- and plasma aided flame retardation.

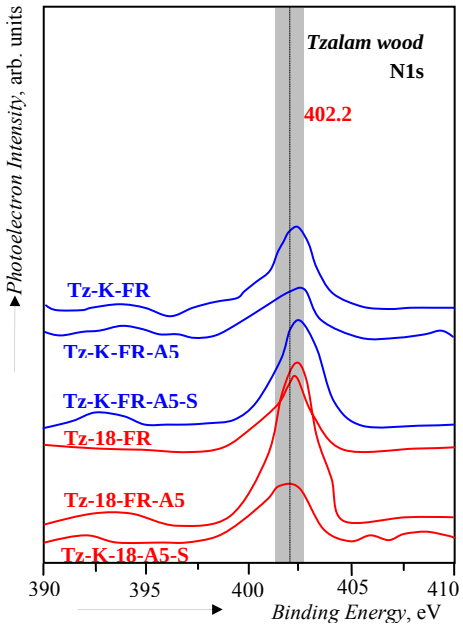

Fig. 8. Nitrogen *N1s* peaks in *XPS/ESCA* spectrums of *Tzalam* heart wood samples after non- and plasma aided flame retardation.

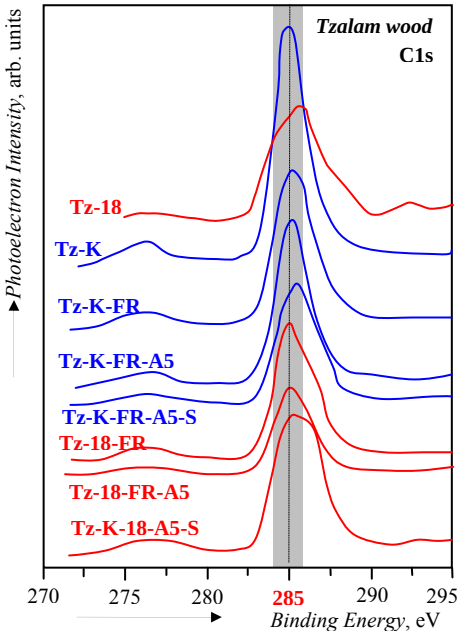

Fig. 7. Carbon *C1s* peaks in *XPS/ESCA* spectrums of *Tzalam* heart wood samples after non- and plasma aided flame retardation.

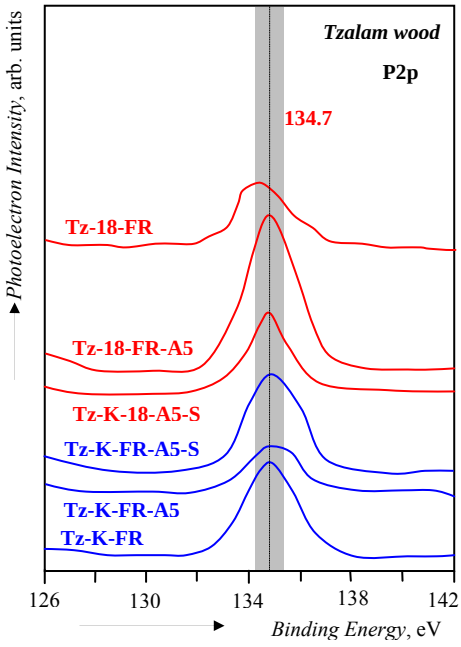

Fig. 9. Phosphor *P2p* peaks in *XPS/ESCA* spectrums of *Tzalam* heart wood samples after non- and plasma aided flame retardation.

frequency (50 Hz) and relatively high voltage (18 kV *RMS*; 25 kV *PV*) characterized by the electrical regime of cathode directed streamers. The endurance of the surface plasma-chemical treatment was 60 seconds.

Well-known anionic surfactant (in 5 vol. %: Tza-K/18-FR-A5) and silicon spreader (in 0.01 vol. %: Tza-K/18-FR-A5-S) were used in well-known way for improving the capillary impregnation characteristics performance, [4].

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

Wide and high resolution (*C1s*, *O1s*) *XPS/ESCA* spectra of *Tzalam* heart wood surfaces were obtained after capillary impregnation with phosphor and nitrogen containing flame retardant inorganic solution before (*Tza-K-FR-*) and after plasma (*DBD-*) pre-treatment (50 Hz; 18 kV *RMS*: *Tza-18-FR-*).

3. Experimental Results and Discussion

Wide *XPS/ESCA* spectra of *Tzalam* heart wood surfaces, Fig. 1, reveal clearly two facts: *i* – wide *XPS-* spectra significantly differ in the intensity of the photoelectron emission – with the highest intensity is the spectrum of bare *Tzalam* wood sample – *Tza-K*, and with lowest intensity is the spectrum of plasma-aided flame-retardant treated sample *Tza-18-FR-A5-S*; *ii* – clearly outlined are the characteristic peaks of the used nitrogen and phosphor containing flame retardant – in the nitrogen area (*N1s*: 402.2 eV) and in the phosphorus area (*P2p*: 134.7 eV); *iii* – clearly defined are two of the peaks which determine the surface oxidation degree of the wood and the water amount, immobilized on the surface – carbon peak (*C1s*: 285 eV) and oxygen peak (*O1s*: 532.5 eV).

X-ray photoelectron spectroscopy as a non-destructive surface chemical analysis technique provides valuable data on chemical surface composition and re-organization. The thickness of the studied surface layer reaches 5 to 10 nm. This means that the data refer only to this layer or the surface of the flame retarded wood samples.

Elemental composition of *Tzalam* heart wood surfaces after capillary impregnation with phosphor and nitrogen containing flame retardant solution before (*Tza-K-*) and after plasma pre-treatment (*Tza-18-*) determined from wide *XPS*-spectra is characterized by a significant increase of the content of phosphor (*P2p*) and nitrogen (*N1s*) in the surface layer after flame-retardant capillary impregnation, Table 1.

It is interesting that after plasma pre-treatment is registered the maximum value in the surface concentration of phosphorus when using impregnation flame retardant aqueous solution without spreader – 11.260 at. % phosphor and 9.426 at. % nitrogen for *Tza-18-FR-A5*. This is more than two (2.11) times for phosphorus and more than one and a half (1.75) times for nitrogen compared to traditional capillary impregnation (*Tza-K-FR*) with the same amount of the used flame retardant, Table 1.

The use of adjusted by anionic surfactant or anionic surfactant and silicon spreader impregnation aqueous solutions does not allow to achieve higher phosphorus and nitrogen concentrations in the surface layer of the wood samples – 6.721 at. % for phosphor and 8.046 at. % for nitrogen, Table 1.

From our previous studies, [5], it is well known that by introducing of the same amount of impregnation flame retardant aqueous solution the highest speed of absorption of the solution and suppression of the flame burning (flaming) is observed in the case of *Tza-18-FR-A5* and Tza-18-FR-A5-S samples.

Most flame-retardant treatments delay ignition, reduce heat release, and reduce flame spreading. The used flame-retardant chemicals shift the thermal degradation to the low temperature pathway of noncombustible gases and a greater proportion of char residue. The reactions are acid catalyzed hydrolysis of the cellulose and hemicellulose. Chemicals dehydrate the wood and increase the condensation and cross-linking of the carbon skeleton. Other possible mechanisms for fire retardancy include in addition the formation of an insulating carbon layer, increased dissipation via conduction of heat away from heat source, endothermic reactions to absorb heat, and release of radicals that inhibit flaming combustion, [1].

Namely the higher amount of phosphorus in the surface layer of the wood sample is crucial in the construction of the protective charcoal layer which does not let oxygen towards the area of pyrolysis, and vice versa of combustion gases, that maintain the spreading of the flame burning. This is supported by the increased intensity of the photoelectron emission at 134.7 eV (*P2p*), Fig. 9, in all samples, obtained by plasma aided impregnation. On the contrary, the intensity of the photoelectron emission at 402.2 eV (*N1s*), Fig. 8, is significantly lower in these samples of *Tzalam* wood.

XPS-analysis of the bare *Tzalam* wood surface reveals by the *nO/nC* and *nC1/nC2* ratios the existence of cellulose (*nO/nC* = 0.83; *nC1/nC2* = 0), lignin (*nO/nC* = 0.10; *nC1/nC2* = 1), and resin and extractive materials (*nO/nC* = 0.33; $1 < nC1/nC2 < 10$) on the wood surface. The ratio *nO/nC* was closed to 0.1 than to 0.33 - 0.17. The ratio *nC1/nC2* was greater than one - *nC1/nC2* = 2.3779 > 1.000. These results demonstrate conclusively the importance of resin and extractive materials for the plasma-chemical wood surface modification. It could be argued that an additional role in element alternation of *Tzalam* wood surface play the lignin - the ratio *nO/nC* was closed to 0.10 but greater than 0.10 and the ratio *nC1/nC2* was greater than 1.0 but closed to 1.0, Table 1 and 2.

This is what happens with these two ratios after plasma-chemical pre-treatment and capillary flame-retardant impregnation treatment: *i* – the ratio *nO/nC* increases toward 0.170 as it takes values in a very large range – from 0.3274 to 1.2329, Table 1; *ii* – the ratio *nC1/nC2* significantly decreases toward 2.3779 and takes values in a relatively narrower range – from 2.0408 to 1.4071, Table 2.

The direct comparison of the intensity of the flow of photoelectrons in the carbon peak area *C1s* and of oxygen peak *O1s*, Fig. 6 and 7, allows us to reveal two characteristic features of plasma-aided capillary impregnation treatment of wood surface: *i* – after capillary flame retardant impregnation treatment the intensity of the photoelectrons in the area of the two characteristic peaks *C1s* and *O1s* is significantly reduced for the both types of test samples – with and without plasma pre-treatment; *ii* – after plasma–aided capillary flame retardation treatment the test samples show in all cases reduced intensity of photoelectrons in the area of both peaks *C1s* and *O1s* and the *Tza-18-FR-A5-S* sample shows the minimum intensity.

This comparison may be done in parallel for both types of the studied test samples – with and without plasma pre-treatment, as the analysis includes high-resolution *XPS*-spectra field of carbon *C1s* oxygen *O1s* peaks. The results obtained from the conducted spectral analysis allow us to monitor the surface reorganization after capillary flame-retardant impregnation, Fig. 2 and 4, and after plasma-aided capillary impregnation, Fig. 3 and 5.

It is evident from the data in Table 2 and 3, different type of *oxygen to carbon bonding* (C-O; C=O; O-C-O; or O-C=O) was observed not only before and after plasma-chemical pre-treatment. *Tzalam* wood samples indicate the impact of the capillary impregnation conditions on the wood surface chemistry and re-organization.

The *Sum (C2;C3)* covers quantitatively all different type of oxygen to carbon bonding - C-O; C=O; and O-C-O, Table 2. The alternative *Sum (O1;O3)* covers quantitatively this oxygen to carbon bonding plus H-O-H (water), Table 3.

The difference between *Sum (O1;O3)* and *Sum (C2;C3)* gives the amount of chemically bonding water on the wood surface and the changing after plasma-chemical pre-treatment and capillary flame-retardant impregnation treatment. The surface plasma modification by *DBD* at atmospheric pressure decreases the amount of water on the wood surface but the capillary flame-retardant impregnation treatment increases this amount, Table 3.

After cold plasma pre-treatment the amount of water in the wood surface layer (to 5-10 nm) significantly increases but after flame-retardant impregnation treatment this increase is much more impressive. Although plasma-chemical functionalization of wood surface increases the hygroscopicity of treated wood, it should be emphasized that the hygroscopicity of the impregnated with inorganic salts wood grows to similar values regardless of whether it had been plasma treated or not. However, the wood sample with the greatest amount of water in the surface layer is the one subjected to plasma-aided capillary impregnation treatment – *Tza-18-FR-A5*, Table 3.

It is well known that wood treated with inorganic flame-retardant salts containing phosphor and nitrogen can be more hygroscopic than untreated wood. The increases in equilibrium moisture content will depend upon the plasma pre-treatment, chemicals, surfactants and spreaders, level of chemical retention, and size and species of wood involved. Higher moisture content increases problems with corrosion of fasteners.

Conclusion

The studies on plasma-aided flame retardation, carried out on *Tzalam* wood (*Lysiloma bahamensis*), allow us to evaluate the potential of *XPS/ESCA*-analysis for revealing the change in the surface chemistry and the reorganization degree after plasma-chemical pre-treatment and capillary flame retardant impregnation with inorganic salts containing phosphor and nitrogen.

By means of *XPS/ESCA*-analysis it is possible to analyze the chemistry and the surface reorganization to a depth of 5 to 10 nm. This enables the efficiency of plasma-aided capillary impregnation treatment to connect not only with technological results such as high absorption rate of flame retardant aqueous solution, a greater depth of absorption and a larger amount of the absorbed flame retardant, but also with the higher amount of the phosphorus in the surface layer of the wood.

It should be reminded once again that the conducted experiment was carried out with one and the same amount of imported impregnation solution containing phosphorous and nitrogen inorganic compounds. Only under these conditions it may be said that the effectiveness of phosphor and nitrogen containing flame retardant is due to the increased content of phosphorus in the surface layer (form 5 to 10 nm).

Of course, the use of the full technological capacity of the plasma-aided capillary flame retardant impregnation includes the introduction of a greater amount of active inorganic salts in the wood surface layer. The carried out experiment shows that even with one and the same amount of imported aqueous solution containing flame retardant, it may be implemented regimes technologically where the phosphorus content in the surface layer is substantially greater.

The results obtained from *XPS/ESCA* analysis very well reveal the increased hygroscopicity of wood samples after phosphorus and nitrogen containing flame retardants impregnation.

The results obtained from *XPS/ESCA* analysis on wood from the tropical *Tzalam* tree are valuable precisely because due to the high resin content and easily migrating components towards the surface this wood is hardly amenable to impregnation, especially with relatively concentrated aqueous solutions of inorganic salts (round 30 wt. %). In such cases plasma-aided capillary impregnation very often remains the only technology, which can effectively bring the right amount of the active substance in the surface layer.

Acknowledgements

The authors gratefully acknowledge the financial support of Technical University - Sofia, for the Research Project 132ПД0051-01.

References

[1] White. R. H. and M. A. Dietenberger. Wood Products: Thermal Degradation and Fire. *Encyclopedia of Materials: Science and Technology.* Elsevier Science Ltd., 2001; ISBN: 0-08-0431526; pp. 9712-9716.

[2] Dineff, P., D. Gospodinova, L. Kostova, T. Vladkova, and E. Chen., *Plasma aided surface technology for modification of materials referred to fire protection*, Problems of Atomic Science and Technology, Series Plasma Physics (14), 2008, 6, pp. 198÷200.

[3] P. Dineff, L. Kostova. *Method for Plasma Chemical Surface Modification*. H05H 1/24, Bulgarian Patent Publication No.: BG 66022 B1; International Patent Publication No.: WO Patent 2006/133524 A2; Priority Date: 14.06.2005 (BG No. 109189).

[4] Динев, П., Д. Господинова, И. Аврамова. *Електродни конфигурации на бариерен разряд и ефект на повърхностно химично активиране*. XIX. Международна конференция по авангардни материали и обработки „АМО'09", 25÷27 юни, 2009, Кранево, България. Сборник с доклади, ДМТ-Продукт, 2009, стр. 191÷196.

[5] Господинова, Д., И. Иванов, П. Динев, Л. Велева, А. Гутиерес, *Плазмено подпомогната огнезащита на дървесина от ТЦАЛАМ (Lysiloma Bahamensis) - I и II.* Годишник на Техническия университет - София, София, България, Том: 62, Кн.: 4, 2012, стр. у