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PLASMA AIDED FLAME RETARDATION OF WOOD, WOODEN PRODUCTS AND CELLULOSIC MATERIALS

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 and capillary activity and improves such characteristics of the impregnation process as the penetration depth, speed of solution spreading and adsorption, and capacity of adsorbed solution. X-ray photoelectron spectroscopy (XPS) was applied to study the changed surface composition after plasma pre-treatment. The surface compositions of solid wood products, paper and board are critical to their end use performance. XPS is a powerful non-destructive surface analytical technique which provides valuable data on chemical surface composition and surface reorganization after plasma-chemical pre-treatment. The binding energy as a main characteristic of the atoms was used for elemental identification. Thermal analysis (TGA, DTA and DSC) was used to characterize the impact of the plasma surface activation on flame retardancy of Douglas fir wood. This study was developed as a part of large investigation on chemically activated wood surface and flame retarded wood.
Key words: plasma aided flame retardation, dielectric barrier discharge, surface modification

1. INTRODUCTION

The plasma aided flame retardation of wood, wooden products and cellulosic fibrous materials has been conceived and developed as a result of a new plasma aided process of capillary impregnation. The ability of the wood matrix to adsorb water is thus of critical importance for the wood water solution capillary impregnation. The plasma-chemical surface pre-treatment modifies the chemical activity of wood surface as well as the its capillary activity and improves such technological characteristics of the impregnation process as penetration depth, speed of solution spreading and adsorption, and specific quantity of adsorbed solution per unit of surface area. This fact allows using the plasma aided retardation as a finishing process and applying it "in situ". A system consists of plasma device and several applicators have been created to produce cold technological plasma through dielectric barrier discharge (*DBD*) at atmospheric pressure and room temperature [1, 2].

It is well known that heat treatments and machining reduce the wood wettability and chemical activity by modifying this water-reactive matrix in different ways. Earlier we found that the cold plasma pre-treatment of soft wood, like pine (*Pinus sylvestris*), improves technological characteristics such as solution spreading and adsorption speed, as well as specific amount of the adsorbed flame retardant. In this way, the plasma pre-treatment of pine wood improves its flame retardation and allows "in situ" performance of the procedure [3, 4].

Douglas fir is a largely used wood in a lot of building constructions, flooring, timbers, but its flame retardency by capillary (or surface) impregnation is difficult, due to its relatively high density and surface inactivation. Therefore, the impregnation of this type of wood is often performed under high pressure or vacuum, the procedure requiring complicated apparatus and machines and a simple geometric shape of the constructions, i.e. lumbers or timbers. In addition, the flame retardency is successful at flame retardant penetration depth of 10÷15 mm but than an unacceptable decrease (down to 30 %) of the wood mechanical parameters arises, [5].

The effect of plasma pre-treatment onto the wood surface activation (or functionalization) was investigated as well as the effect of different surfactant systems onto the ionic activity of the impregnation solution, both aimed at improvement of Douglas fir wood flame retardation. Some experimental results of the investigation are presented here: alteration the wood surface chemical composition or surface functionalization as a result of the cold plasma pre-treatment at atmospheric pressure and room temperature monitored by X-ray photoelectron spectroscopy (*XPS*-) analyses; solution impregnation on bare or plasma pre-treated Douglas fir wood without or with additional surfactant to the impregnating solution; and the change of wood thermal degradation as a result of a flame retardation under different conditions monitored by thermal analysis (*TGA, DTA, DSC*).

2. EXPERIMENTAL

Douglas fir soft wood (*Pseudotsuga menziesii,* Canada), density of 678 g/cm^3 and moisture content of 7.8 %) and pine soft wood (*Pinus Sylvestris*, Bulgaria) were used in this investigation. Test samples with size of 5x30x150 mm were manufactured by heard wood for capillary impregnation.

On the basis of the prior art as well as on a own former experience in the plasma aided impregnation of wood and wooden materials, [6, 7], an oxidative surface plasma pre-treatment on a part of the test samples was performed for 1 min in a dielectric barrier air discharge at atmospheric pressure at industrial frequency (50 Hz) and two voltage values – 10 and 15 kV, oxygen and ozone or nitrogen oxides (NO_x) respectively non-equilibrium cold plasma, and increased frequency (10 kHz) at voltage of 10 kV.

The *DBD* plasma system consists of a coplanar shaped rectangular electrodes with a glass barrier (thickness of 3 mm) arranged closeness to grounded electrode with operating distance between high voltage electrode and barrier of 6 mm, Fig 1a. The *DBD* was assured by two different - low frequency (50 Hz) and high frequency (10 kHz), voltage generators. The wood samples were disposed in operating volume and

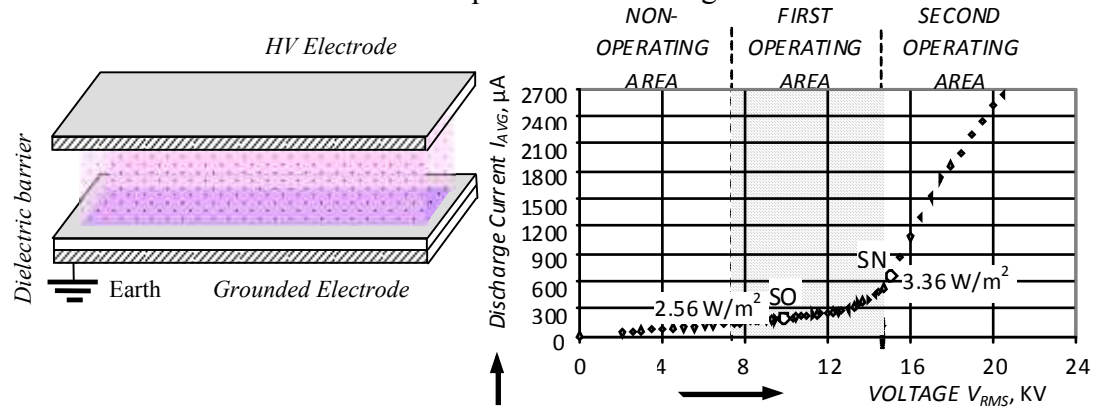treated for one minute at chosen frequencies and voltages.

Fig. 1. *Dielectric barrier discharge coplanar electrode system with one glass barrier (**a**), static volt-ampere characteristic I_{AVG} - V_{RMS}, and regimes of plasma pre-treatment at industrial frequency of 50 Hz - SO: voltage of 10 kV (RMS); real specific power 2.56 W/m^2, and SN: voltage of 15 kV (RMS); real specific power 3.36 W/m^2 (**b**).*

A tendency to the halogen containing flame retardants replacement by halogen-free ones is observed lately because of the toxicity of the halogens, [8]. A halogen-free, phosphorus and nitrogen containing flame retardant was used in this investigation in form of 30 w. % water solution. The impregnating water solution (*FRIS*, dry substance of 30 w. %; phosphorus content of 13 w. %, pH = 7÷8 and density of 1.14 g/cm^3) was based on a halogen free phosphorus and nitrogen containing flame retardant. A new flame retardant product on the basis of ortho-phosphorous acid, urea and ammonia was studied.

Wood inactivation is a surface phenomenon affecting just a thin outer layer of wood. An inactivated wood surface does not absorb capillary well an impregnating solution containing phosphorous compound as flame retardant. Plasma-chemical surface activation (functionalization) with an effective participation of ionic surfactants and silicone spreaders eliminates the inactivation-impregnating problem creating a protective flame retardant layer on the wood surface. The air plasma treatment gives different results from the nitrogen and oxygen treatments. Anionic surfactants (*AS*, "*Aniticrystallin A*", Chimatech, Ltd., Bulgaria) in quantity of 5 vol. %, or silicone super spreader (*SSP*, Y-17113, Momentive Performance Materials GmbH & Co. KG, Germany) in quantity of 0.1 vol. %, as well as their combinations, were used to control the ion activity of the flame retardant impregnation water solution. The capillary impregnation was performed on bare (for comparison) or plasma pre-treated Douglas fir wood samples at atmospheric pressure by spraying of the corresponding flame retardant solution (390 ml/m^2).

X-ray photoelectron spectroscopy is a very powerful non-destructive surface analytical technique which provides valuable data on chemical surface composition and surface reorganization after plasma-chemical pre-treatment. *XPS* is a surface chemical analysis technique that can be used successful to analyze the surface chemistry of a material in its "as received" state, or after some treatment such as cold plasma pre-treatment. The binding energy is a characteristic of the atoms, which can be used for elemental identification. *XPS*-analysis in 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 degrees. *XPS*-spectra are obtained by irradiating a material with a beam of X-rays while

simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the analyzed material. *XPS* detects all elements with an atomic number (Z) of 3 (lithium) and above. This limitation means that it cannot detect hydrogen ($Z=1$) or helium ($Z=2$). Detection limits for most of the elements are in the parts per thousand (ppm) ranges, [9].

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 pre-treatment, [10]. This study was developed as a part of large investigation on plasma-chemical activation and flame retardance of wood surface, [1, 3, 4, 6, and 7].

Thermal analysis – thermogravimetric analysis (*TGA*), differential scanning calorimetry (*DSC*), and differential thermal analysis (*DTA*), was performed in air at a heating rate of 50 ^{0}C /min in the temperature range of 25÷1200 ^{0}C using *Perkins-Elmer* equipment. The sample size was of about 3.0 mg.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The studied plasma aided capillary impregnation is based on both a plasma-chemical pre-treatment of the wood surface and the impregnating flame retardant solution ion activity optimization. An increase of the wood capillary activity and the impregnating solution adsorption speed and capacity would allow performance of a good enough flame porous wood surface retardance [1, 2 and 7].

The dielectric barrier discharge surface activation or the expected surface reorganization and alternation of the chemical composition as a result of the plasma pre-treatment as well as the flame retardant solution impregnation were monitored directly by *XPS*-analysis, and the bare and flame protected Douglas fir wood thermal behavior – by T*GA*, *DTA*, and *DSC*-analysis.

3.1. *DBD* activation effect and surface chemical composition by *XPS*-analysis

The inactivated wood surface usually contains the same components as the bulk but the proportions among polysaccharides, lignin and extractives could be substantially different as a result of the different conditions and methods of surface formation. It is well known, [5] that a high temperature expose during drying, cutting, etc. inactivates the wood surface due to physical and chemical modifications that leads to reduced ability of solutions to properly wet and penetrate. Thus, an inactivated wood surface makes difficult the impregnation. The plasma treatment leads to surface cleaning and changing the chemical composition those impacts on the surface wettability. Oxidative cold plasma treatment accompanied with an accumulation of oxygen containing groups on the surface usually increases its polarity and wettability. The effect depends on the operation conditions [1, 7].

Similar changes are the basis of the expecting *DBD* surface activation effect on the Douglas fir wood surface, plasma pre-treatment in three types of dielectric barrier discharge in air at atmospheric pressure was performed: *i*) *DBD* at industrial frequency (50 Hz) and relatively low voltage (10 kV) at which the major active species arise from ionized and activated air oxygen; *ii*) *DBD* at industrial frequency and relatively high voltage (15 kV) at which the major active species arise from ionized and activated air oxygen and nitrogen, Fig. 1b; *iii*) *DBD* at high frequency (10 kHz) and relatively low voltage (10 kV) at which the major active species arise

from both: ionized and activated air oxygen with the cold plasma higher density [10, 11].

The surface chemical composition change after such plasma pre-treatment was monitored by comparative *XPS*-analysis of non-treated and plasma pre-treated Douglas fir wood samples. Some results are presented in Table 1. The *XPS*-wide spectra of pre-treated and untreated wood samples show three peaks at 285.0, 533.2, and 400.4 eV attributed respectively to C_{1s}, O_{1s} and N_{1s}. The elements carbon (C), oxygen (O) and nitrogen (N) were detected on the investigated Douglas fir wood surfaces. The nitrogen, detected on the non plasma treated - control sample, is most probably adsorbed on the surface from the ambient air. The atomic percents of the elements as well as of the carbon components (i.e., C1, C2 C3 and C4) were determined from the wide and high-resolution *XPS*-spectra - Table 1 and 2.

The presented in Table 1 data confirm the expected oxidation of the Douglas wood surface: *i*) the surface oxygen content of all Douglas fir wood plasma treated samples is higher (25.5÷31.7 at. %) as compared to the non-treated sample (21.79 at. %); *ii*) the total percentage of the surface carbon bonded to oxygen (the last column, Table 2) is also higher (41.9÷44.6 %) for all plasma treated samples compared to (35.9 %) the non-treated one; *iii*) the *nO/nC* ratio (Table 1) of plasma treated samples is higher (0.34÷0.46) compared to (0.28) the non-treated one. The plasma pre-treatment provoked oxidation of the Douglas wood surface is similar but in different degree to the plasma enhanced oxidation of the pine wood surface, Table 1 and 2.

According to *Kazayawoko* et al., high-resolution spectrum of the carbon peak C_{1s} show the presence of different chemical states, or classes, of carbon on the bare wood surface (K). The C_{1s} peak was observed to consist of four main components, which were ascribed to four classes of carbon atoms present on wood surface: C1 (285.0±0.4 eV) – carbon atoms bonded to carbon or hydrogen atom; C2 (285.6±0.4 eV) - carbon atoms bonded to a single non-carbonyl oxygen atom; C3 (288.0±0.4 eV) - carbon atoms are bonded to two non-carbonyl or to single carbonyl oxygen atom, and C4 (289.5±0.4 eV) – carbon atoms ascribed to the carboxyl oxygen group. C1, C2 and C3 states of carbon are the main components of the C_{1s} peak whereas the C4 component detects in some cases, Table 2, [10].

Analysis from the *XPS*-measurement results, Table 1 and 2, and carbon (C_{s1}) and oxygen (O_{s1}) peaks, Table 2 and 3, leads to the conclusion that the air plasma-chemical surface modification of wood at atmospheric pressure by *DBD* is a useful and effective method for surface chemical activation of inactivated wood (*Douglas fir, pine*) by oxidation of lignin, resin and extractive materials. That is right because the *XPS*-analysis of the bare Douglas fir surface reveals by the nO/nC ratio (0.28) the existence of lignin (about 0.33), and resin and extractive materials (about 0.10) on the wood surface.

It is evident from the data in Table 2, different type of oxygen to carbon bonding (C-O; C=O; O-C-O; or O-C=O) is observed for the plasma pre-treated under different operation conditions Douglas fir wood samples, indicating the impact of the operation conditions on the wood surface oxidation. It was observed that C_{1s} peak consists of a maximum increased C2 carbon state (C-O) and increased C3 state (C=0, O-C-O) on the functionalized Douglas fir surface (*SO*) at first operating condition of *DBD* (50 Hz, 10 kV). The second operating condition of *DBD* (50 Hz, 15 kV) increases to maximum level the C3 (C=0, O-C-O) and C4 carbon state (O-C=O), but decreased the C2 state. The third operating condition of *DBD* (10 kHz, 10 kV)

increases C2, C3 and C4 together, Table 2. The air plasma-chemical functionalization of Douglas fir wood surface examined in the daylight of the alteration of carbon to oxygen bonding holds out opportunities for its controlling by the operating condition of *DBD* pre-treatment.

Table 1. *Elemental composition of Douglas fir and pine heart wood surfaces before (K) and after plasma pre-treatment (SO, SN, SHF) determined from wide XPS-spectra.*

Kind of Wood: Density, kg/m³	Samples			Chemical Surface Composition, at. %				
			Peaks	**C**	**O**	**N**	**nO/nC**	**nN/nC**
Heart Douglas Fir wood (*Pseudotsuga menziesii*, Canada): 678 *kg/m³*	*DBD* Pretreated	K (Non-Treated)		77.69	21.79	0.52	0.28	0.0067
		SO	10 kV (50 Hz)	68.30	31.70	0.00	0.46	0.0000
		SN	15 kV(50 Hz)	69.10	29.90	1.00	0.43	0.0145
		SHF	10 kV (10 kHz)	74.00	25.50	0.50	0.34	0.0068
Heart Pine Wood (*Pinus Sylvestris*, Bulgaria: 371 *kg/m³*	*DBD* Pre-treated	K (Non-Treated)		74.80	24.40	0.70	0.33	0.0094
		SO	10 kV (50 Hz)	70.10	28.50	0.60	0.41	0.0086
		SN	15 kV(50 Hz)	70.40	29.00	0.60	0.41	0.0058
		SHF	10 kV (10 kHz)	73.50	26.10	0.40	0.36	0.0049

The high-resolution spectrum of the oxygen peak O_{1s} includes the following main four different chemical states of oxygen atom on the wood surfaces: O1 (531.5±0.4 eV) – O=C; O2 (532.5±0.4 eV) – O-H; O3 (533.0±0.4 eV) – O-C or H-O-H; and O4 (534.5±0.4 eV) – not defined [13]. The carbon and oxygen states are relevant – C3 to O1 and C2 to O3, but the amounts of C2 and C3 and O1 and O3 aren't corresponding. The found difference is due to the absorbed water (H-O-H) in the surface layer, Table 3.

XPS findings revealed that *DBD* pre-treatment increases the nO/nC ratio by oxidation of the Douglas fir surfaces and decreases the nC1/nC2 ratio, Table 2.

3.2. *DBD* activation effect and surface chemical composition after plasma aided impregnation determined by *XPS*-analysis

The plasma treatment leads to surface cleaning and change its chemical composition that impact to the surface wettability and water solution impregnation. The surface chemical composition change after such plasma-aided impregnation with water solution containing phosphorous and nitrogen flame retardant was monitored by comparative *XPS*-analysis of non-treated and plasma pre-treated Douglas fir wood samples. For this investigation we use non-corrected and corrected by anionic surfactant (of 2, 5, 10 and 20 vol. %; *AS2*, *AS5*, *AS10* and *AS20*) and flame retardant solution (*FRIS*). Some results are presented in Table 4.

The appearance of nitrogen (N) and phosphor (P) on the flame surface retarded by *FRIS* samples in fixed ratio nN/nP (0.58) is not a surprise having for that the flame retardant on the surface (up to 5 nm in depth) contains nitrogen and phosphorous as element and the nitrogen on the surface of the bare wood is too small (0.58 at. %) compared to the nitrogen (5.7 at. %) on the surface after impregnation, Table 4 and 1.

The ion activity correction of the impregnating *FRIS* by the supplementation of an anionic surfactant did not change materially the ratio nN/nP – form 0.58 to 0.61 at. %, but decreases the nitrogen from 5.7 to 3.7 at. %, and the phosphorous from 9.8 to 6.1 at. % on the surface, Table 4 and 5. The phosphor and nitrogen containing flame

retardant penetrated in depth of the wood matrix without changing its chemical composition.

Table 2: *Carbon peak C_{s1} components or proportions of oxygen and carbon functional groups of Douglas fir and pine hard wood surfaces before (K) and after plasma pre-treatment (SO, SN, SHF) determined from high-resolution XPS-spectra.*

Kind of Wood: Density, kg/m³	Samples		Carbon peak C_{s1} components, %					
			C1 (C-C or C-H)	**C2** (C-O, C-OH)	**C3** (C=O, O-C-O)	**C4** (O-C=O)	**nC1/nC2**	$\sum_{2}^{3} C_i$
			(285.0 ±0.4 eV)	(286.0 ±0.4 eV)	(288.7 ±0.4 eV)	(289.5 ±0.4 eV)	-	-
Heart Douglas Fir wood (Pseudotsuga menziesii, Canada): 678 kg/m³	*K* (Non-Treated)		64.1	31.0	4.9	0.0	2.068	35.9
	DBD Pre-treated	SO	55.4	38.9	5.7	0.0	1.424	44.6
		SN	58.1	23.5	12.8	5.6	2.472	41.9
		SHF	57.5	35.0	6.2	1.3	1.643	42.5
Heart Pine Wood (Pinus Sylvestris, Bulgaria: 371 kg/m³	*K* (Non-Treated)		54.1	34.8	8.8	2.3	1.554	45.9
	DBD Pre-treated	SO	50.9	37.2	9.8	2.1	1.368	49.1
		SN	45.2	40.4	11.9	2.6	1.119	54.8
		SHF	45.4	40.1	12.0	2.5	1.132	54.6

Table 3: *Oxygen peak O_{s1} components of Douglas fir heart wood surfaces before (K) and after plasma pre-treatment (SO, SN, SHF) determined from high-resolution XPS-spectra.*

Kind of Wood: Heart Douglas Fir wood (Pseudotsuga menziesii, Canada)	Samples		Oxygen peak components, %					
			O1 (O=C)	**O2** (O-H)	**O3** (O-C; H-O-H)	**O4** not-defined	C2+C3	O1+O3
			(531.5 ±0.4 eV)	(532.5 ±0.4 eV)	(533.0 ±0.4 eV)	(534.5 ±0.4 eV)	%	%
	K (Non-Treated)		0.0	0.0	100	0.0	35.9	100.0
	DBD Pre-treated	SO	3.2	0.0	91.8	5.0	44.6	95.0
		SN	5.5	59.9	34.6	0.0	36.3	40.1
		SHF	12.2	51.2	36.6	0.0	41.2	48.8

Table 4: Elemental composition of Douglas fir hard wood surfaces flame retarded by capillary impregnation (FR) and plasma-aided capillary impregnation determined from wide XPS-spectra.

Impregnated Samples		Chemical Surface Composition, at. %				
	Peaks	C	O	N	P	nN/nP
FR	Non-treated	46.6	37.9	5.7	9.8	0.58
Pl10-FR	DBD pre-treated	53.8	32.3	4.8	9.1	0.53
Pl15-FR		61.9	30.0	3.5	4.6	0.76
PlHF-FR		52.2	35.4	5.3	7.1	0.75

The other way about the plasma-aided impregnation with basic *FRIS* is DBD pre-treatment changed materially the ratio nN/nP – from 0.58 to 0.53 (0.76 and 0.75) at. %, Table 4. Generally, the phosphorus and nitrogen at. % are simultaneously reduced (below 9.8 at. %) if an ionic surfactant presents in the *FRIS*, Table 4 and 5. These results indicating that the phosphorus and nitrogen content reduction on the surface is most probably due to quick impregnating solution penetration in the wood bulk. The more significant decrease of the phosphorus and nitrogen content on the surface with the increase of the anionic surfactant amount, Table5, compare samples PlHF-FR-AS2 - PlHF-FR-AS20), as well as the almost constant nN/nP ratio on the compared surfaces confirms this supposition.

It is not the same case of the plasma pre-treated wood or the plasma-aided impregnation. The comparison of the surface elemental composition of Douglas fir samples impregnated with the basic *FRIS* (without surfactant addition) plasma pre-treated and non pre-treated shows some significant differences in the phosphorus and nitrogen content. Non treated and plasma pre-treated phosphorus and nitrogen content surfaces varying in dependence on the plasma treatment operation conditions, Table 4 and 5. It should be marked also, that nN/nP ratio of the plasma non pre-treated sample (of 0.58) differs significantly from the plasma pre-treated samples.

These facts indicate that some chemical interactions between the plasma pre-activated wood surface and the flame retardant occurs changing otherworld almost constant nN/nP ratio. If we use plasma pre-treatment that will be alters the chemical reactivity of the wood surface by oxygen containing group's accumulation (Table 1 and 2) and most probably they interact somehow with the flame retardant.

Table 5: Elemental composition of Douglas fir wood surfaces flame retarded by anionic surfactant (AS) aided capillary impregnation (FR-AS) and plasma-aided capillary impregnation (Pl-FR-AS) with different amount of surfactant (2, 5, 10, and 20 vol. %) determined from wide XPS-spectra.

Impregnated Samples		Chemical Surface Composition, at. %				
	Peaks	C	O	N	P	N/P
FR-AS2	Non-treated	62.0	28.2	3.7	6.1	0.61
Pl10-FR-AS2	DBD-LF pre-treated	66.2	25.9	2.9	5.0	0.58
Pl15-FR-AS2		50.2	36.8	5.6	7.4	0.76
PlHF-FR-AS2	DBD-HF pre-treated	53.2	34.0	5.8	7.0	0.83
PlHF-FR-AS5		59.8	30.8	4.1	5.3	0.77
PlHF-FR-AS10		53.3	36.2	3.6	6.9	0.52
PlHF-FR-AS20		58.9	35.7	2.2	3.2	0.69

3.3. DBD activation effect determined by thermal (TGA, DTA and DSC) analysis

Solid materials do not burn directly - they have to be first decomposed by heat (pyrolysis) to release flammable gases. Visible flames appear when these flammable gases burn together with oxygen in the air. If solid materials do not break down into

gases, than they will only smolder slowly and often self extinguish particularly if they char and form stable carbonaceous barrier which prevents flame access to the underlying material. Materials like wood burns vigorously because once ignited, the generated heat breaks down the long-chain molecules to smaller fragments transpiring as gases. The gas flame maintains itself by the action of high energy spaces (that is H^+ and OH^- in the gas phase) decomposing the molecules to free carbon that can react with the air oxygen to "born" CO, generating heat energy. The different types flame retardants inhibit the flaming process on different mechanisms, [8].

The most common and best known fire retardant methods for wood are based on pathway pyrolysis changing. In this simple and inexpensive method, wood is treated with a substance that enhances the pyrolysis reaction of cellulose through the pathway leading to char formation mainly. Ideally, the reactions would proceed so that the cellulose decomposes to char and water: $(C_6H_{10}O_5)_n \rightarrow n (6 C + 5 H_2O)$, [12].

It is well known, [8, 12], that the phosphorus containing flame retardants act efficiently in the solid phase of the burning material. Under heating they deliver polymeric forms of the phosphoric acid that forms glassy layer inhibiting the pyrolysis process by braking down the material charring and flammable gases release necessary to feed the flame. The delivered phosphoric acid is able to do both, to suppress a glucosans formation and to block the flammable volatile products release. Substances influencing on pyrolysis often react with the hydroxyl group attached to the sixth carbon atom of cellulose molecule, leading eventually to the stabilization of the structure through the formation of a double bond between the fifth and sixth carbon atom. This action mode leads to predominant char formation than flammable gases. Hence the pyrolysis with char formation gets a priority in presence of the phosphorous flame retardant. The char barrier layer grows and thus cut off the head and oxygen transfer to pyrolysis zone. At the same time it doesn't allow the flammable gases to pass trough and flame spreading is stopped. The thickness and morphology of the "char barrier" determine the flame retardancy quality. The phosphorus and nitrogen containing flame retardants combine the flame retarding mechanisms of both phosphorus and nitrogen compounds with synergetic effects reinforcing their function.

Thermal analysis – *TGA, DTA* and *DSC*, was employed for evaluation of the influence of wood treatment on pyrolysis and combustion. Thermal analysis gives us basic information on the thermal decomposition mechanism, ignition and burning as well as data on the wood treatments and modification.
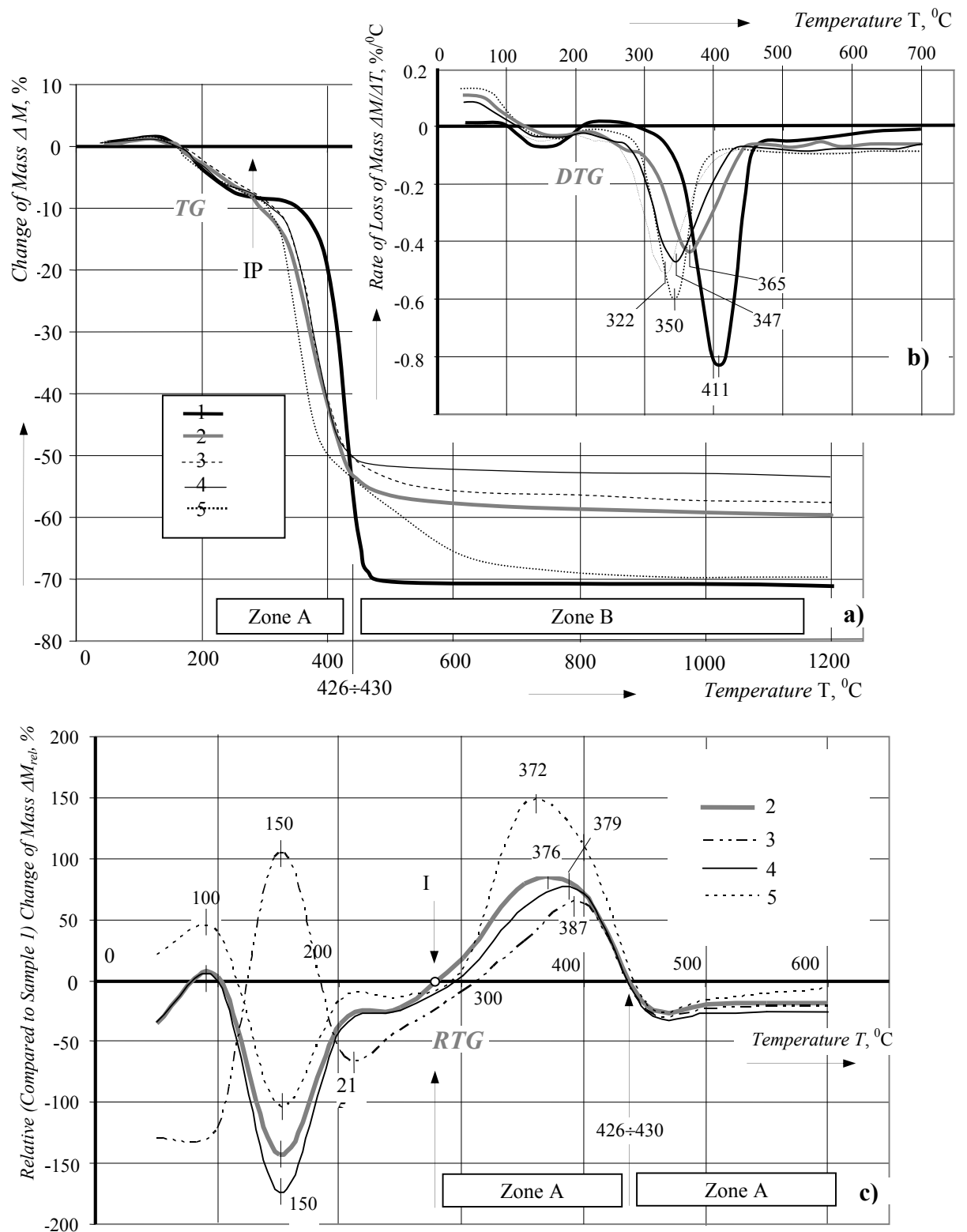
Fig. 2: *Thermal analysis – TGA **(a)** and DTGA **(b)** spectra, of bare Douglas fir wood (1), flame retarded wood by capillary FRIS impregnation with 2 vol. % of anionic surfactant (2) and flame retarded wood by plasma-aided capillary impregnation at different operating rate of DBD pre-treatment: 3 – low frequency (50 Hz) DBD at 10 kV; 4 - low frequency (50 Hz) DBD at 15 kV, and 5 - high frequency (10 kHz) DBD at 10 kV (at 50 ⁰C/min). The relative change of mass **(c)** is obtained in comparison with the bare Douglas fir wood.*
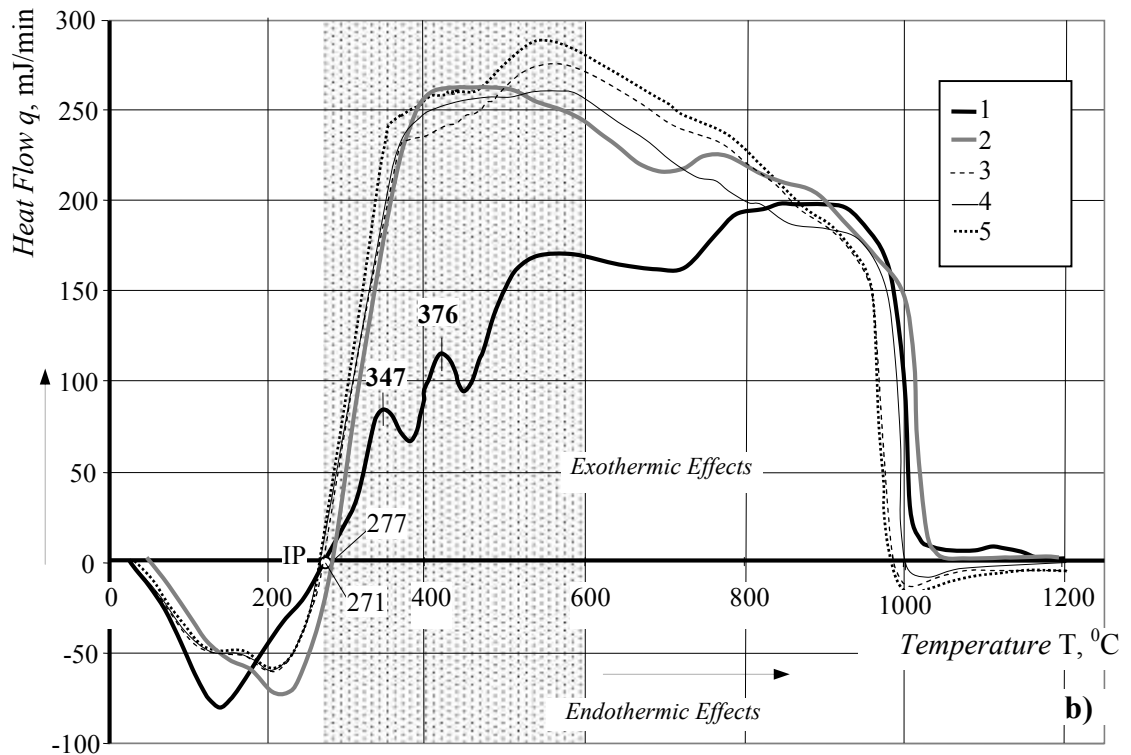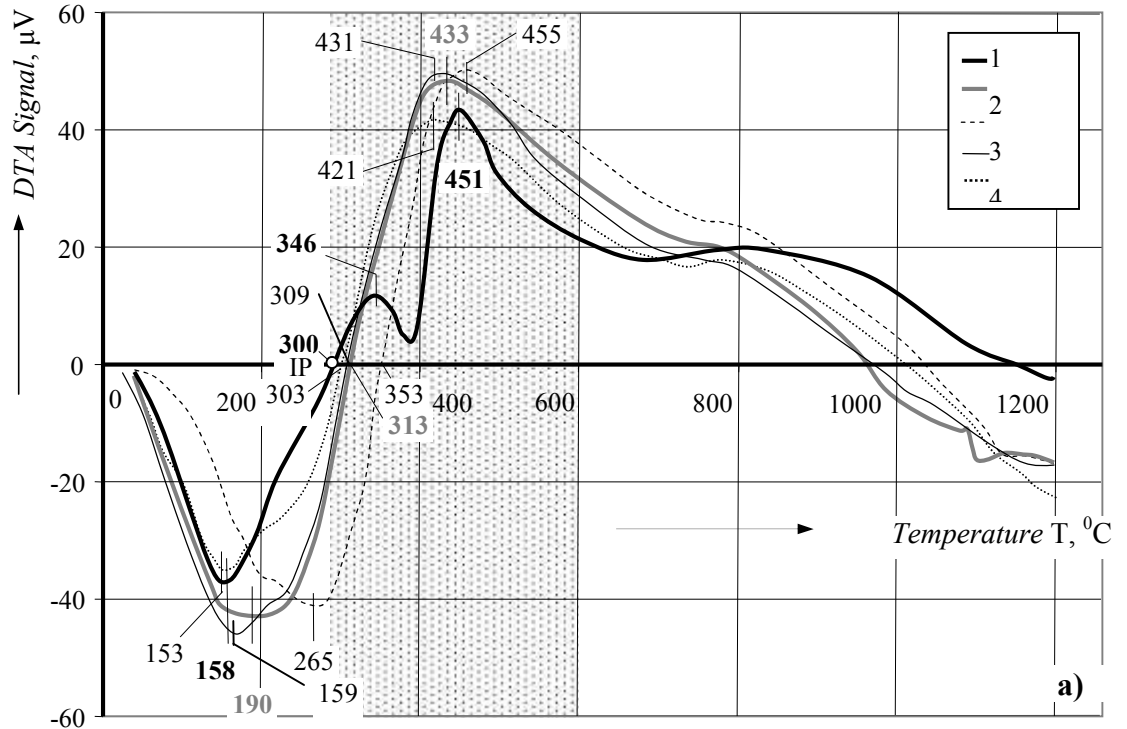
Fig. 3: *Thermal analysis – DTA (a) and DSC (b) curves, of bare Douglas fir wood (1), flame retarded wood by capillary FRIS impregnation with 2 vol. % of anionic surfactant (2) and flame retarded wood by plasma-aided capillary impregnation at different operating rate of DBD pre-treatment: 3 – low frequency (50 Hz) DBD at 10 kV; 4 - low frequency (50 Hz) DBD at 15 kV, and 5 - high frequency (10 kHz) DBD at 10 kV (at heating rate of 50 ^{0}C/min).*

A clear distinction should be made between fire barrier assemblies which utilize fire resistant materials (rated) and flame or fire retarded materials (indexed). The

terms seem alike and are often confused but are quite distinct. Fire rated materials prevent ignition over fixed length of time. Fire retarded materials, on the other hand, will ignite. They slow down; however, the flame spread and smoke development of the burning material. Fire retardant materials are typically used by the building codes regulation for interior finish materials. A low flame spread materials will not necessarily improve the performance of a fire rated assembly.

When a wood product burns at a constant rate of heat release per unit area, the boundary between the pyrolysed material and the intact wood, i.e. the pyrolysis front, proceeds to the wood in depth direction. Since all pyrolysing wood can be considered to char, the *charring rate* corresponds to the propagation rate of the pyrolysis front. Charring rate is an essential quantity for the fire resistance of wooden structures, because the wood under the char layer preserves its original properties. Important factors for the wood charring rate are the density, the external heat flux and the moisture content. Charring rate decreases with increasing density according to the power law – Douglas fir wood belong to the class of high density woods (678 kg/m^3), i.e. its charing rate is about 1 mm/min. Charring rate is not generally much influenced by fire retardants. However, the char yield is usually increased quite a lot, that might contribute to the protection of the wood core, [12].

However, the correlation between results of thermal analysis - *TG* (*DTG*), *DTA* and *DSC*, and the real wood fire behavior was not established yet, [13]. Usually the thermal analysis is carried out at thermodynamically stable equilibrium, i.e. the temperature rate below to the 4÷10 ^{0}C/min range. The real fire reach the flashover (about 600°C) for ten minutes and the relevant heating rate is essentially higher – form 50 to 60°C/min. One better approximation to real fire might be a thermal analysis at increased rate of heating (50°C/min) closer to the real fire condition.

TG and *DTG analysis* curves of the above described samples are presented in Fig. 2a. The mass loss at all studied samples in the first temperature zone (up to the ignition point) is slight due to a release of a small amount of inflammable volatile substances and the differences between the samples indicate their different dehydratation and decomposition.

The intense pyrolysis of the non-protected wood sample, Fig. 2a, *TG*-curve 1, in the flaming zone (the first after the ignition point) is accompanied with a very sharp mass loss (more than 60 %) due to a lot of low molecular weight flammable volatile products formation. Whereas suppressed flaming and started below ignition point (*IP*) glowing with coal char formation is visually observed for all flame retarded samples, Fig. 2a. *TG*-curves 2÷5 are accompanied with less mass loss compared to the control wood sample. The *DBD* pre-treatment effect on the flame retardency for different operational conditions, Fig.2b, *DTG*-curves 3÷5 was expressed by the appearance of the main peak at lower temperatures (322, 347, 350°C) comparing to the flame retarded wood sample (365 ^{0}C), i.e. it reinforced the flame retardency effect, in comparison with bare wood (411°C). The formation of protective barrier char layer started earlier and finished before flaming start of the bare wood, Fig. 2b. This *DBD* pre-treatment effect attended with a well expressed growth of the loss of mass compared to the bare wood. The built char barrier (in temperature zone A) retarded the loss of mass of flame retarded samples after 426÷430 ^{0}C (zone B), Fig.2c. The total mass loss at the 600ºC of *DBD*-aided flame retarded samples was 52, 55 % for low and 66 % for high frequency *DBD*, against 58 % for flame retarded wood samples and 71 % for bare wood.

DSC and *DTA* curves of the flame retarded wood, Fig. 3, curves 2÷5, to that of the

bare wood, curve 1, demonstrate significant alterations of the thermal effects and head flow in all described temperature zones. Zones indicating in this way that the used flame retardant and *DBD* pre-treatment influenced all steps of the wood pyrolysis and burning.

The comparison of curve 2 and curve 1, Fig. 3a, shows: *i*) a slight shift of the *IP* to the higher temperature – from 300ºC for the bare wood and up to 303÷350ºC for the flame protected one; *ii*) the appearance of a enlarged endothermic peak at 190ºC for the flame retarded wood is evidently connect to the thermal decomposition of the used flame retardant; *iii*) the observed bare wood flaming peak at 346 (347)ºC is suppressed and absorbed by an enlarged charing peak at 433ºC for flame retarded wood. Such large peak relevant to the building of the protective char barrier is observed too after the *IP* at different temperature for *DBD* pre-treatment flame retarded wood: 421 and 431ºC for low and 455ºC for high frequency *DBD*. A significant difference was finding - the using *FRIS* leads to an enlarged total exothermic effect in comparison with the bare wood, Fig. 3b. At the same time *DBD* pre-treatment improves the flame retardancy and diminish total exothermic effect but it remains higher than the bare wood one.

CONCLUSION

As a result of the carried out experimental investigations on the *DBD* pre-treatment effects on the Douglas fir surface chemistry and flame retardancy after capillary (surface) impregnation with phosphor and nitrogen containing flame retardant we are in position for the following main conclusion:

1. The Douglas fir wood surface is very sensitive to the ionic activity of the impregnation water solution;

2. The Douglas fir wood plasma or *DBD* pre-treatment have significant influence over the ionic surface balance of the wood, keeping its amphoteric character;

3. *DBD* pre-treatment at different operation conditions has as result the change of the surface chemistry – an oxidation of the wood surface is realized;

4. Both the cold plasma pre-treatment (or chemical surface modification) and the control of the *FRIS* ionic activity by different surfactants (spreaders) offer some possibilities for the improvement of capillary (surface) impregnation process and the flame retardancy of Douglas fir wood;

5. Plasma-aided capillary impregnation process with ion active flame retardant water solutions give new opportunities for improvement of the flame retardancy of wood and wood products and can be adopted as a universal approach to the impregnation processes.

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