PLASMA-AIDED SURFACE FINISHING FOR FLAME RETARDATION OF WOOD THROUGH THE USE OF SURFACTANTS

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Abstract: *The plasma aided flame retardation of wood, wooden products and cellulosic fibrous materials has been conceived and developed as a result of plasma aided process of capillary impregnation with nitrogen- and phosphorous containing water solution. The surface pre-treatment in non-thermal equilibrium atmospheric pressure plasma substantially alters its electrical, chemical and capillary activity, thus improving some basic characteristics, such as penetration depth, water solution spreading and wicking, liquid adsorption capacity. This study has been developed as part of a large investigation on plasma-chemically activated wood surface and its capillary impregnation with nitrogen- and phosphor flame retardant containing water solution. It has been used to reveal and illustrate the impact of some ionic and silicon surfactant. The experimental studies of some chemical, ion and capillary activity changes of three species of rain-forest Mexican heart wood surfaces using selected surfactants and spreaders show that they have substantial contribution to the effective plasma-aided capillary impregnation processes.*

Keywords: ATMOSPHERIC OR AIR DIELECTRIC BARRIER DISCHARGE (*DBD*), FLAME RETARDATION OF WOOD, PLASMA-AIDED SURFECE FINISHING PROCESS, SURFACTANT, SILICON SURFACTANT, SPREADER.

1. Introduction

Surface finishing is the art in manufacturing having to do with substrate new useful texture, morphology, and properties. It is well known that these processes may range from deposition, removal, or cleaning. Such processes are conducted inside sophisticated tools that can be limited in their flexibility for research and development.

Corona surface treatment

Since 1951 *corona treatment* (*Verner Eisby*, *Vetaphone A/S*, Denmark) is currently the most used surface finishing technique in the industry for treating surfaces of polymer films and textiles. "*Corona*" is a *Dielectric Barrier Discharge* (*DBD*) in air at atmospheric pressure and room temperature. This kind of electric discharge is controlled by a dielectric barrier and is in form of streamers distributed in a haphazard manner over the surface, [4].

The *Corona surface treatment or Atmospheric pressure plasma treatment (APPT)* is essential in converting processes. A quality *Corona* is necessary to obtain sufficient wetting and adhesion on plastic films or metallic foils before the printing, laminating or coating. Due to the low surface energy (surface wettability, adhesion) of stock materials the printing press or laminator cannot run at full speed. *Corona systems* are used to create fresh clean surface that is receptive to ink, glue and lacquer. This *Corona technique* has proved to be both highly effective, cost-effective and can take place "*in-line*", [4].

In general the following rule is true: *"A material will be wetted, if its surface energy is higher than the surface tension of the liquid"*. If not, there will be wetting and adhesion problems.

Durability of corona treatment or how long does it last?

Over time the obtained surface energy (*dyne-level*) will decrease and it can be necessary to corona treat the material again *just before use*. Also storage conditions and temperatures can affect the decay of the corona treatment result.

Generally, the more difficult a material is to treat the quicker it is likely to decay with time. It has been established that polymer film with very high slip additives (over 1200 ppm) can be totally resistant to printing just 24 hours after treatment, and it may be necessary to process the film immediately following treatment, or boost *the treatment in line* with the printer. Material which has not been treated under extrusion can be difficult to treat afterwards. Therefore it is recommended to treat film just after the extrusion, and then use a *refreshment treatment* just before the liquid/media is supplied to the surface, [4].

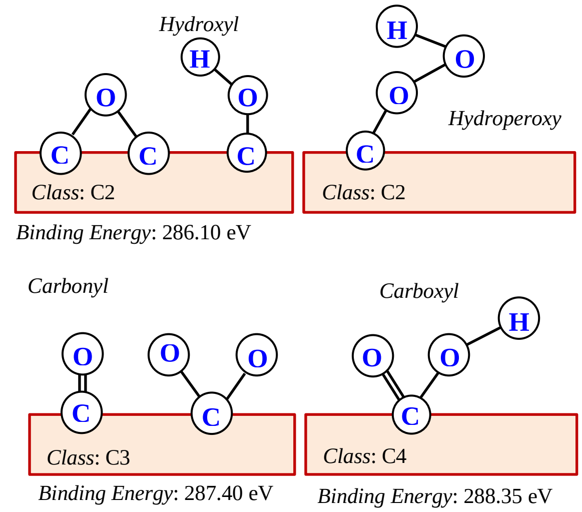


Fig. 1. Changes of wood surface chemistry after plasma surface *DBD* (corona) pre-treatment (or functionalization). Classes of various oxygen containing functional groups according to number of oxygen atoms bonding to carbon atom: *Class C2*, with one oxygen atom (C-O; C-OH); *Class C3*, with two oxygen atoms (O-C-O) or with one carbonyl oxygen atom (C=O); *Class C4*, with one carbonyl and one non-carbonyl oxygen atoms (O-C=O), (after *Kazayawoko*, 1998).

EASI-Plasma improvement

However, on some materials the *atmospheric pressure plasma effects* are limited and have a relatively short life time. *Long time surface functionalization* are achieved by using a *DBD*-plasma and adding small quantities of dopant gas for functionalization in a pure nitrogen atmosphere (*Enhanced Atmospheric Surface*

Improvement or *EASI-Plasma* treatment, *Vetaphone A/S*, 2001). The *EASI-Plasma* is more homogeneous and "*softer*" than Corona, with low heat impact to the surface and it enables the realization of a versatile controlled surface chemistry. Consequently it can be considered as a *gas primer replacing* efficiently both the use of corona treatment and liquid primer. Hydrophobic, hydrophilic or anti-fog surface properties can also be achieved with a 1 to 50 nm thin coating, [4].

Plasma surface pre-treatment "out line" or "in situ"

The *plasma-aided flame retardancy* of wood and wooden products has been developed as a result of creating new *functional coating* containing phosphor and nitrogen flame retardant. The *flame retarded coating* was built by new *plasma-aided surface finishing process* of capillary impregnation. The so called "*open time*" between plasma pre-treatment and capillary impregnation can reach up to 24 hours or the capillary impregnation is not obligatory to follow the plasma pre-treatment immediately such as corona treatment, [1].

Plasma-aided finishing process comprises of: *i* - plasma-chemical (*DBD*-) surface pre-treatment for increasing the wood surface energy and altering its chemical, electrical (ionic) and capillary activities; *ii*- change of ionic activity and surface tension of flame retardant (*FR*) containing water solution by ionic and non-ionic aqueous surface-active agents (surfactants), and in general for improvement some characteristics of the capillary impregnation process such as solution spreading and wicking speed, as well as the amount of the penetrated (sorbed) flame retardant. In this way, the plasma pre-treatment of wood improves wooden flame retardancy, Fig. 2, [1, 2, and 3].

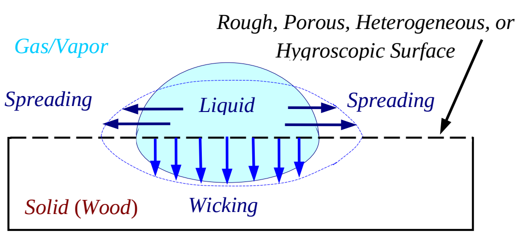


Fig. 2. *Model of wetting phenomena - the wetting phenomena on a real surface can be involved by: i - spreading of liquid over a solid surface; ii - wicking of liquid into the porous solid (such as wood).*

The *Sessile Drop Technique* is a method for characterization of wood (solid) surface energy. The measured contact angle and the known surface energy of the probe liquids are the parameters which can be used to calculate the solid sample surface energy. Time-depending change of contact angle θ of a flame retardant (*FR*-) water solution as it advances slowly over a non-ideal wood surface (e.g., not chemically homogeneous, rough or not perfectly smooth, porous and hygroscopic as in the case of most practical wood surfaces) can by determined by contact angle measurements 2 and 24 hours after *DBD*-treatment, [5].

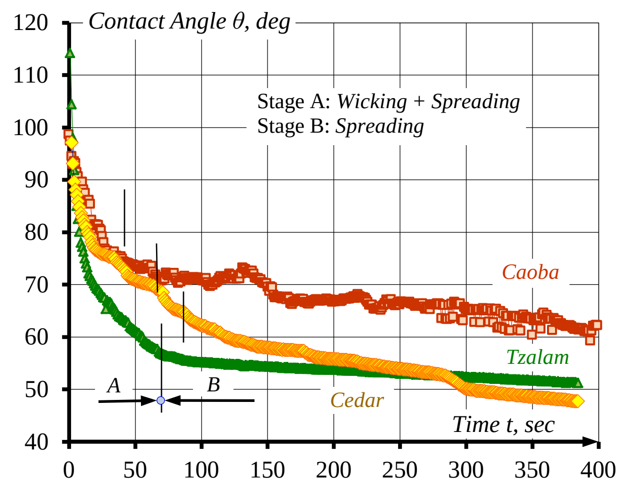
The objective of this paper was to study the effect of some surfactants, [1, 2 and 3], on plasma-aided finishing process and more precisely on the "*open time*" between plasma treatment and capillary impregnation. Reaching an open time of 24 hours is a guarantee for the successful implementation of this plasma-aided process "*in situ*" or out of the production line. This study has been developed as part of a large research on plasma-chemically finished wood surfaces and flame retarded constructive wood products.

2. Experimental Investigation

A *low contact angle* indicates a high solid surface energy, and a high or sometimes complete degree of wetting. For example, a contact angle of zero degrees will occur when the droplet has turned into a flat puddle: this is called complete wetting. The droplet was deposited by a syringe pointed vertically down onto the wood surface and a high resolution camera captures the image, which can then be analyzed by using image analysis software. By taking pictures incrementally as the droplet advances over the surface the user can acquire a set of data to get a good time-depending change of the contact angle, [2, 3].

The apparatus used for this study was a KRÜSS Drop Shape Analyzer DSA 30. Precisely controlled tempering and humidity chambers help to provide a realistic modeling of the process conditions. Measuring range (referred to image analysis): contact angle - 1÷180 deg; surface free energy - 0.01÷1000 mN/m. Measurement resolution: contact angle - 0.1 deg; surface free energy - 0.01 mN/m. Test volume of the used sessile drop: 20 μl (20 mm^3). Zoom: 6.5 times and image resolution: 45 pix/mm, [2].

A way to experimentally determine liquid capillary penetration (spreading and wicking) is to look at the contact angle (θ). If $\theta = 0$ deg, the liquid completely wets the substrate; if $0 < \theta < 90$ deg, high wetting occurs; if $90 << \theta < 180$ deg, low wetting occurs; if $\theta = 180$ deg, the liquid does not wet the substrate at all.



Stage A: *Wicking + Spreading*			
Duration, sec	86	47	100
Initial Contact Angle, deg	114.2	92.2	97.1
Final Contact Angle, deg	51.3	74.3	47.9
Wood Samples	*Tzalam*	*Cedar*	*Caoba*

Fig. 3. *Time-depending changes of contact angle θ of basic FR-water solution as it advances slowly over the non-ideal bare (non-plasma treated) wood surfaces. There are two very different stages of wetting behavior. The first stage A or wicking stage is completed in time of 100÷150 sec and the contact angle rapidly decreases.*

The determination of surface free energy and its disperse and polar fractions are performed after contact angle measurement with three well known probe liquids: *Water* (bifunctional); *Ethylene glycol* (acidic), and *n-Hexadecane* (neutral), [2, 3].

On the basis of prior art, as well as on our own former experience in plasma-aided capillary impregnation of wood, [1, 2], an oxidative (nitrogen oxides, NO_x) surface plasma pre-treatment has been applied on two sides of the test samples for 60 sec in a *DBD* at industrial frequency (50 Hz) and 18 kV (*RMS*) or about 25.4 kV (*PV*) voltage.

Studies of *cold plasma functionalization phenomena,* 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 rain-forest Mexican heart wood were investigated: two hardwoods, *i - Tzalam* (*Lysiloma bahamensis*); *ii - Caoba Mahogany* (*Swietenia macrophylla*); and one softwood, *White Cedar* (*Cupressus Lusitanica*).

Results and discussion

The contact angle is amended in a specific way in the study of porous media - at the initial moment it has a given value, significantly lower after 5 sec and substantially (with 30 to 50 %) less after the first or wicking stage, Fig. 2 and 3, Table 1.

Table 1. Contact angle *θ measured dynamically by Sessile Drop Test with water – the contact angle increases dramatically after 24 hours and there is no significant wetting effect (see Caoba Mahogany).*

Sessile Drop Test (*Water*)			
Samples	*Tzalam*	*Cedar*	*Caoba*
Bare Wood Samples			
Initial Contact Angel *θ*, deg	126.7	98.9	92.1
Contact Angel *θ* (5 sec), deg	97.6	92.6	71.3
Contact Angle *θ* (300 sec), deg	56.7	62.0	65.0
Plasma Pre-Treated Samples			
Contact Angle *θ* (2 hours), deg	19.2	70,2	21.3
Contact Angle *θ* (24 hours), deg	84,0	78.2	101,0

Reason for this characteristic for porous media (wood and wooden products) amending of contact angle, surface free energy and polarity, Table 1 and 2, is the presence of wicking that accompanies spreading and dominates in the first or wicking stage (A) of wetting and capillary impregnation process, Fig. 3.

Table 2. Calculated total surface free energy and its fractions of bare rain-forest Mexican wood samples 5 sec (Stage A: wicking+spreading) and 300 sec (*Stage B*: spreading) after droplet deposition on surface at about 22 ^{0}C.

Polar fraction and polarity (*P*) of bare wood samples increase substantially (more than two times) after completion of the

Sessile Drop Test (*Bare Wood Samples*)					
Total Surface Free Energy, mN/m					
Sample	Zisman Theory	Equation of State (EOS) Theory		Fowkes Theory	Wu Theory
5 sec after droplet deposition on wood surface					
Tzalam	30.24	31.50	± 4.61	29.77	42.46
Cedar	32.50	33.04	± 7.54	30.89	44.11
Caoba	33.10	32.58	± 8.89	29.91	42.95
300 sec (5 min) after droplet deposition on wood surface					
Tzalam	34.74	42.25	± 12.82	46.46	59.19
Cedar	34.74	38.20	± 10.10	38.94	52.88
Caoba	34.74	38.91	± 10.28	40.82	54.52

Fractions of Total Surface Free Energy						
	Fowkes Theory			Wu Theory		
Sampl e	Polar Fraction	Disperse Fraction	Pola rity, *P*	Polar Fraction	Disperse Fraction	Pola rity, *P*
	mN/m	mN/m	-	mN/m	mN/m	-
5 sec after droplet deposition on wood surface						
Tzalam	4.74	25.04	0.159	7.53	34.93	0.177
Cedar	4.04	26.85	0.131	6.90	37.21	0.156
Caoba	2.66	27.25	0.089	5.21	37.73	0.121
300 sec (5 min) after droplet deposition on wood surface						
Tzalam	17.67	28.78	0.380	19.45	39.74	0.329
Cedar	10.16	28.78	0.261	13.14	39.74	0.248
Caoba	12.04	28.78	0.295	14.78	39.74	0.271

wicking stage of capillary impregnation. This means that the initial contact angle affects the participation of both basic processes - wetting and capillary impregnation, which run in parallel and at different speeds. For the same purpose due to technical impossibility to measure the initial contact angle it should be measured after 5 sec from droplet deposition on the surface.

The study of the plasma treated wood surfaces makes it possible to show the effects of increase of surface free energy and of surface polarity after plasma treatment. However after 24 hours this effect decreases considerably, Table 3.

The effects of plasma aided *FR*-impregnation can be easily studied by using suitable solutions and registering the kinetics of change of the contact angle, Fig. 4, 5 and 6.

By following a similar manner it is possible to study plasma aided flame retardancy enhanced with surfactants, object of the current study, Fig. 4, 5 and 6.

Table 3. Calculated total surface free energy and its fractions of bare rain-forest Mexican wood samples 5 sec (Stage A: wicking + spreading) and 300 sec (*Stage B*: spreading) after droplet deposition on surface at about 22 ^{0}C. Sessile drop measurement with three test flame retardant (*FR*-) liquids 2 and 24 hours after plasma (*DBD*-) treatment. *NA* – unable to be measured.

Sessile Drop Test (*Plasma Treated Samples*)					
Total Surface Free Energy, mN/m					
Sample	Zisman Theory	Equation of State (EOS) Theory		Fowkes Theory	Wu Theory
Bare wood samples (5 sec)					
Tzalam	30.24	31.50	± 4.61	29.77	42.46
Cedar	32.50	33.04	± 7.54	30.89	44.11
Caoba	33.10	32.58	± 8.89	29.91	42.95
2 hours after plasma treatment					
Tzalam	NA	47.08	± 21.17	57.27	63.18
Cedar	NA	43.47	± 21.75	49.25	56.20
Caoba	27.90	35.41	± 7.44	37.96	40.62
24 hours after plasma treatment					
Tzalam	30.33	32.68	± 4.96	34.77	37.54
Cedar	31.44	29.17	± 7.65	32.08	34.81
Caoba	29.77	33.89	± 5.48	36.07	38.77

Components of Total Surface Free Energy						
	Fowkes Theory			Wu Theory		
Sample	Polar Fraction	Disperse Fraction	Pola rity	Polar Fraction	Disperse Fraction	Pola rity
	mN/m	mN/m	-	mN/m	mN/m	-
Bare wood samples (5 sec)						
Tzalam	4.74	25.04	**0.159**	7.53	34.93	**0.177**
Cedar	4.04	26.85	0.131	6.90	37.21	**0.156**
Caoba	2.66	27.25	**0.089**	5.21	37.73	**0.121**
2 hours after plasma treatment						
Tzalam	32.09	25.18	**0.560**	38.88	24.30	**0.615**
Cedar	24.41	24.84	**0.495**	33.25	22.95	**0.592**
Caoba	10.99	26.96	**0.290**	14.35	26.27	**0.353**
24 hours after plasma treatment						
Tzalam	6.50	28.27	0.187	9.78	27.76	0.260
Cedar	2.66	29.42	**0.083**	5.95	28.87	0.171
Caoba	8.19	27.88	0.227	11.46	27.31	0.296

Conclusion

The obtained results allow us to make the following conclusions:

- The *Sessile Drop Technique* enables direct study of the kinetic of liquid penetration by image analysis with *FR*- water solutions – basic phosphor and nitrogen containing *FR*-solution and *FR*- solution with different surfactants;

- The *Initial Contact Angle* or this at 5 sec after the droplet deposition on the surface may be used as a common feature of wetting and penetration process without separating the two parallel running elementary processes to wicking and spreading;

- The term defined as *superhydrophilic* is used for surfaces with a liquid contact angle of less than 20 degrees, where droplets spread out nearly flat. *Plasma aided flame retardancy* is a new technology that provides this effect at open time up to two and more hours but can't provide this effect after 24 hours after plasma treatment.

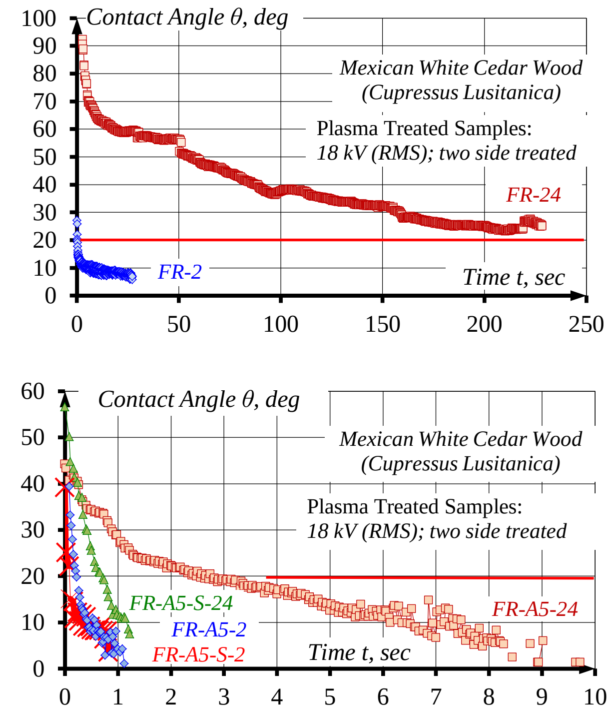


Fig. 4. Time-depending change of contact angle θ of basic (*FR-*) phosphor and nitrogen containing flame retardant water solution, *FR-* solution with 5 vol. % anionic phosphor surfactant (*FR-A5-*), and *FR-A5* solution with 0.1 vol. % siloxane surfactant (*FR-A5-S-*) as they advance slowly over the surface of plasma treated wood samples 2 and 24 hours after plasma surface pre-treatment (-2; -24).

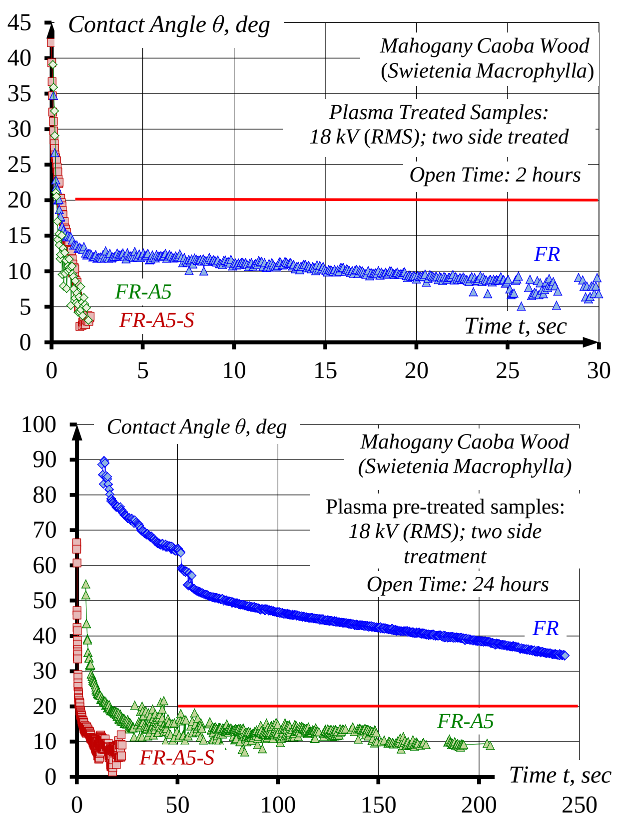


Fig. 5. Time-depending change of contact angle θ of basic water solution (*FR-*), *FR-* solution with 5 vol. % anionic phosphor surfactant (*FR-A5-*), and *FR-A5-* solution with 0.1 vol. % siloxane surfactant (*FR-A5-S-*).

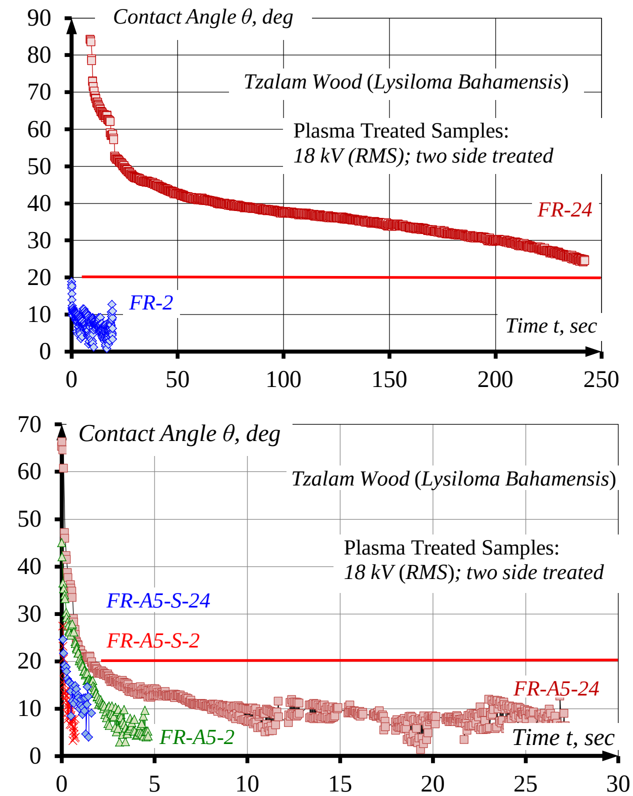


Fig. 6. Time-depending change of contact angle θ of basic (*FR-*) phosphor and nitrogen containing flame retardant water solution, *FR-* solution with 5 vol. % anionic phosphor surfactant (*FR-A5-*), and *FR-A5* solution with 0.1 vol. % siloxane surfactant (*FR-A5-S-*) as they advance slowly over the surface of plasma treated wood samples 2 and 24 hours after plasma surface pre-treatment (-2; -24).

The contact angle remains larger than 20 deg, and for some of the studied wood samples (*Mahogany caoba*) – above 30 deg;

- *Plasma aided flame retardancy* (without surfactants) provides *superhydrophilic* wood surfaces for 2 hours open time at contact angle under 20 deg (even 10 and below 10 deg);

- *Surfactants enhanced* plasma aided flame retardancy enables „open time" up to 24 hours, while in general the contact angle decreases and remains below 10 deg, i.e. these surfaces are still *superhydrophilic* even after 24 hours;

- plasma aided flame retardancy *enhanced with surfactants* permits the implementation of „*in situ*" plasma finishing process.

References

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