# Efficiency Processing Parameter for Plasma-Aided Surface Impregnation:

## III. Plasma Surface Activation

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***Abstract*****—Plasma-aided technique can be used to improve the surface impregnation: materials with low surface free energy were subjected to active plasma pre-treatment in order to increase the surface free energy. The higher the surface free energy of the solid substrate is, the better the capillary impregnation. In general, the following efficiency criterion was found: “Plasma-aided impregnation of a material will be more successful and the material will be more susceptible as the difference between its surface free energy and the surface tension of the impregnation solution is greater than zero”. If not, there will be impregnation problems.**

***Keywords*****— penetration-spreading (*****PS-*****) efficiency parameter, dielectric barrier discharge (*****DBD*****), plasma-aided impregnation, surface free energy (*****SFE*****), surface tension (*****SFT*****), European white pine (*****Pinus Sylvestris*****).**

## I. INTRODUCTION

Plasma-chemical surface activation (oxidation) was used to aid or enhance the surface (capillary) impregnation for flame retardancy of wooden and cellulosic products [1, 2, 3].

Sessile drop technique was used to analyze the plasma-aided surface impregnation efficiency. Measurements of contact angle, surface free energy (*SFE*) of the solid and surface tension (*SFT*) of the liquid were used to quantify the success of the plasma-chemical pre-treatment and activation process of the impregnation [2, 3 and 4].

A new efficiency processing parameter was proposed based on two thermodynamic wetting parameters - the *SFE* of porous wood surface and the *SFT* of the impregnating liquid. It allows to use a new approach in assessing the success and feasibility of the impregnation after applying plasma surface activation and impregnating liquid modified by different surfactants [4].

This paper is part of a large study that covers a consistent research work in the field of plasma aided and enhanced technologies [1, 2, 3, 5 and 6].

## II. THEORETICAL AND EXPERIMENTAL INVESTIGATION

### *A. A new plasma-aided surface impregnation approach*

The proposed new integrated approach, [5 and 6], evaluates the applicability of plasma-aided impregnation via two options which mainly manage this process: *first*, the increase of surface free energy (*SFE*) $\sigma_S$ trough plasma-chemical surface activation; and *second*, the reduction of surface tension (*SFT*) $\gamma_L$ of the impregnating solution by different kinds of surfactants. It is well known that Sessile drop analysis allows these parameters to be quantified [2 and 3].

The liquids are often pulled by porous materials into surface pores and capillaries by the so called capillary action. Penetrant (or wicking), spreading and wetting characteristics are also largely responsible for the ability of the liquid (solution) to fill a breaking defect, void, crack, pore or capillary. The impregnation (and wetting) phenomena on a surface can be represented by: *i* - spreading of a liquid over a porous solid surface; *ii* – penetration (or wicking) of the liquid into the porous media (such as wood) Fig. 1.

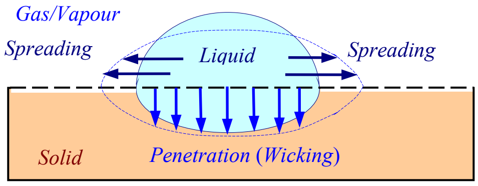

**Figure 1.** Schematic illustration of *Young-Bikerman-Good* dynamic model of wetting phenomena on a rough, porous, heterogeneous, or hygroscopic surface.

The driving pressure characterizing the penetration (wicking, sorption) of the liquid, called *capillary pressure*, is proportional to the “liquid-vapor” *SFT* $\gamma_L$ and inversely proportional to the effective radius $r$ of the capillary opening, it also depends on the contact angle $\theta$ of the liquid on the surface of the capillary:

$$p_C = (2\,\gamma_L \cos\theta)/r = 2\,\Sigma/r. \qquad (1)$$

where $\Sigma = \gamma_L \cos\theta$ is the *adhesion tension* - a wetting characteristic of the media surface.

Using *Young’s Equation*, which relates the contact angle $\theta$ to the interfacial free energy (*IFE*) $\sigma_{SL}$, the adhesion tension $\Sigma$ can be expressed by the surface free energy (*SFE*) $\sigma_S$ as follows:

$$\Sigma = \gamma_L \cos\theta = (\sigma_S - \sigma_{SL}). \qquad (2)$$

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Then the capillary pressure is:

$$p_C = 2/r\,(\sigma_S - \sigma_{SL}). \qquad (3)$$

The capillary pressure $p_C$ reaches its maximum value $p_C\,(max) = 2\ \gamma_L/r$ at complete wetting of the surface when $\cos\theta = 1$ ($\theta = 0^{\circ}$): $\sigma_{SL} = \sigma_S - \gamma_L$ and $\gamma_L = (\sigma_S - \sigma_{SL})$.

The capillary pressure $p_C$ reaches its minimum value or it becomes zero: $p_C\,(min) = 0$, when $\cos\theta = 0$ ($\theta = 90^{\circ}$): $\sigma_S = \sigma_{SL}$.

### B. *Efficiency parameter of the capillary impregnation*

The proposed new integrated approach for evaluating the applicability of plasma-aided impregnation points two options to manage this process integrally: *first*, via surface free energy $\sigma_S$ incensement trough plasma-chemical surface activation; and *second*, via surface tension $\gamma_L$ reduction of the impregnating solution by different kinds of surfactants. Sessile drop analysis helps to quantify these parameters.

The new penetration-spreading or efficiency parameter of the capillary impregnation states that: "*Plasma-aided impregnation of a porous medium (material) will be more successful and the medium will be more susceptible as the difference between its surface free energy and the surface tension of the impregnating water solution is greater than zero*: $0 < PS < \sigma_S$" [5 and 6].

The "solid-liquid" *IFE* $\sigma_{SL}$ is equal to the *PS*- efficiency parameter for complete wetting at $\theta = 0^{\circ}$ ($\cos\theta = 1$): $PS = \sigma_{SL}$. In all other cases of impregnation in the area of high degrees of wetting ($0^{\circ} < \theta < 90^{\circ}$) the *IFE* and *PS*-parameter are not equal $PS \neq \sigma_S$.

The penetration-spreading parameter is the difference between the *SFE* $\sigma_S$ of the porous media and the *SFT* $\gamma_L$ of the impregnating liquid which means that the *PS*-parameter will be better for higher *SFE* and smaller *SFT*.

In porous media, capillary pressure $p_C$ is the tension necessary to squeeze a droplet through a pore throat and to work against the *IFT* $\sigma_{SL}$ between solid and water phases, and $p_C$ is high when the *SFT* $\gamma_L$ of the liquid is higher and the pore diameter $2r$ is smaller. A penetrant liquid will continue to fill a void until there is an opposing pressure that balances the capillary pressure.

Generally, the necessity for a high penetration depth into the pores requires higher capillary pressure which will provide good enough penetration depth, and thus the *SFT* $\gamma_L$ of the liquid should be as high as possible. However, this requirement is contrary to the requirement for obtaining a large positive *PS*-parameter of efficiency ($PS > 0$) which can easily be achieved by reducing the *SFT* $\gamma_L$ of the liquid.

This situation requires a compromise, which needs to ensure the condition for effectiveness of the capillary impregnation process, $PS > 0$, mainly at the expense of maximizing *SFE* $\sigma_S$ through plasma-chemical activation and minimal reduction of the liquid's *SFT* $\gamma_L$. In most cases, the efficiency gains of the capillary impregnation cannot do without the plasma-chemical surface pre-treatment and activation.

## III. EXPERIMENTAL INVESTIGATION

On the basis of our own former experience in plasma-aided capillary impregnation of wood and wooden materials, [1, 2 and 3], an oxidative (nitrogen oxides, $NO_x$) surface plasma pre-treatment in air at atmospheric pressure has been applied on the test samples for 60 secs. A well-known methodology was used for the experiments in this study, [2, 3, 5 and 6].

The *DBD*-technological plasma system consisted of coplanar rectangular shaped electrodes with one glass barrier closely arranged to the high voltage electrode, with a 6 mm air gap. This operative gap defines an effective discharge mode at great surface density of the real power $p_a$ for all selected voltages – 11, 13, 15 and 17 kV rms (15.5, 18.3, 21.2 and 24.0 kV), characterized by a cathode-directed streamer discharge form, Fig. 2.

Sessile drop analysis allows $\sigma_S$, $\gamma_L$ and its difference ($\sigma_S - \gamma_L$) i.e. the *PS*- process efficiency parameter, to be quantified and to propose a relationship that shows the effective process realizations – the *PS*- parameter depends on the *SFE* $\sigma_S$ of the porous medium.

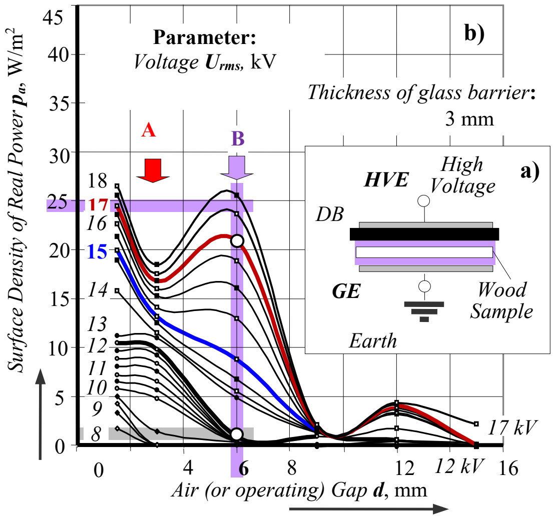

**Figure 2.** Atmospheric pressure plasma or *APP*- treatment of wood sample by non-equilibrium dielectric barrier air discharge in asymmetric coplanar electrode system with one glass barrier (***a***), technological discharge characteristic "*specific surface active power* $p_a$ *– voltage* $U_{rms}$", and regime of plasma pre-treatment at industrial frequency (***b***): ***A*** - transitional mode from electron avalanche to cathode directed streamers; ***B*** – mode of cathode-directed streamers.

The aim of this study was to verify the possibility to evaluate the *PS*- efficiency parameter values for plasma and surfactant enhanced surface impregnation by calculating the *SFE* $\sigma_S$ from the measured values of the contact angle using *Wu* or *Fowkes'* theory and calculation method. All described methods are integrated in the KRÜSS Drop Shape Analysis programs DSA1, [2, 3].

These studies can be considered as an extension of our previous research in this scientific and engineering field [5, 6].

**Table 1.** Sessile Drop Test of *European White Pine* (*Pinus Sylvestris*) Total Surface Free Energy, mJ/m$^2$

| Samples | Theory | | | | |
|---|---|---|---|---|---|
| | Zisman | Equation of State | | Fowkes | Wu |
| (History) | | (EOS) | | Total | Total |
| NPT or 0 kV rms | 28.40 | 22.71 | ± 7.95 | 29.06 | 29.86 |
| PT-11 kV rms | 32.85 | 35.08 | ± 7.88 | 38.26 | 41.16 |
| PT-13 kV rms | 34.19 | 37.26 | ± 9.46 | 41.12 | 43.83 |
| PT-15 kV rms | 34.67 | 43.23 | ± 14.00 | 45.89 | 54.20 |
| PT-17 kV rms | 34.62 | 46.72 | ± 18.75 | 57.11 | 62.23 |
| A24 – *sample aged on air 24 hours after plasma activation;*<br>*All other plasma-activated samples were aged on air 2 hours.* | | | | | |

**Table 2.** Sessile Drop Test of *European White Pine* (*Pinus Sylvestris*) Parts (polar and disperse) of the Surface Free Energy, mJ/m$^2$

| Samples | Theory | | | |
|---|---|---|---|---|
| | Fowkes | | Wu | |
| (History) | Polar | Disperse | Polar | Disperse |
| NPT | 0.07 | 28.98 | 1.47 | 28.39 |
| PT-11 kV rms | 9.59 | 28.67 | 12.97 | 28.19 |
| PT-13 kV rms | 12.46 | 28.66 | 15.55 | 28.28 |
| PT-15 kV rms | 23.99 | 27.03 | 27.84 | 26.36 |
| PT-17 kV rms | 30.95 | 26.16 | 36.88 | 25.35 |
| A24 – *sample aged on air 24 hours after plasma activation;*<br>*All other plasma-activated samples were aged on air 2 hours.* | | | | |

## IV. RESULTS AND DISCUSION

The studied plasma aided or enhanced capillary impregnation of *European white pine* (*EWP*) wood was based on both: plasma-chemical surface pre-treatment, Fig. 2, and surfactant enhanced capillary impregnation. It was expected that the increase of the wood capillary action, penetration speed and capacity would allow achieving a good enough flame retardant performance of porous wood [1, 2 and 3].

The plasma activation (oxidation) by *APP*- surface treatment increases the total *SFE* at the expense of greatly increased polar part (*SFE Polar Part*) of the *SFE*, Table 1 and 2, Fig. 3.

The polar part of the *SFE* increases monotonically with the increased *DBD* voltage and surface density of the real power, Fig. 2.

The penetration-spreading or *PS*- parameter has its positive values ($PS > 0$) for the used flame retardant impregnation solution (*FRIS*) at *DBD* voltages 15 and 17 kV rms, Fig. 4.

It is expected that the *DBD* voltage of 17 kV rms should ensure better impregnation process efficiency as the *SFE* and its polar part are the highest, which determine higher value of the *PS*- parameter, Table 1 and 2, Fig. 3.

However, this prediction is mostly not effective and that can very well be seen in both widely differing cases of capillary impregnation: the impregnation determined by capillary action in the direction of the pores and the impregnation defined by wicking through the capillary walls or transversely to them. The capillary action determines approximately 8-fold greater depth of penetration of the solution against the wicking through the capillary walls, Fig. 5.

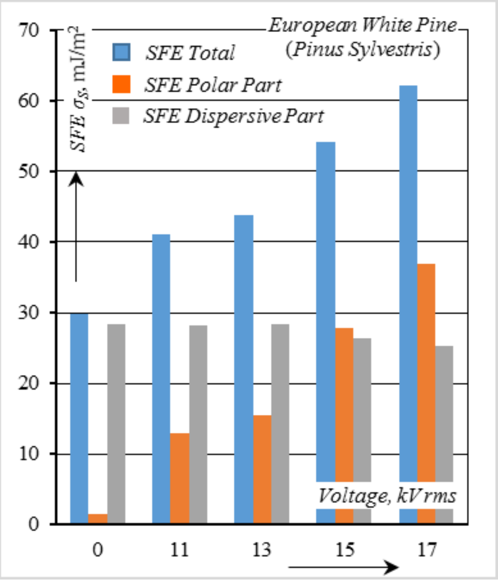

**Figure 3.** Relationship between the *SFT* $\sigma_S$ and its polar and dispersive parts (*Wu's*-theory) and the voltage of *APP*- surface treatment and activation (*EWP*- wood samples) two hours after plasma pre-treatment, Table 1 and 2.

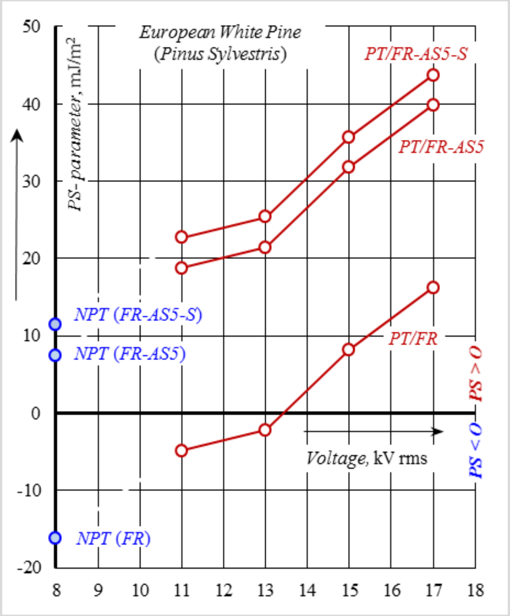

**Figure 4.** Relationship between the penetration-spreading (*PS*-) parameter (*Wu's*-theory) and the *DBD* voltage and the used *FR*- impregnation solutions (*IFRS*): FR- basic *IFRS* containing phosphor and nitrogen flame retardant ($\gamma_L$ = 46.0 mJ/m$^2$), FR-AS5: basic *IFRS* modified by an anionic micelle-forming surfactant of 5 vol. % ($\gamma_L$ = 22.4 mJ/m$^2$), and FR-AS5-S: *FR-AS5- IFRS* modified by a neutral siloxane surfactant (spreader) of 0.1 vol. % ($\gamma_L$ = 18.5 mJ/m$^2$).

In general, the wicking through the capillary walls is essential for the impregnation process. The greatest penetration depth of the solution was observed at 15 kV rms despite our expectation that it would happen at 17 kV rms, Fig. 5b.

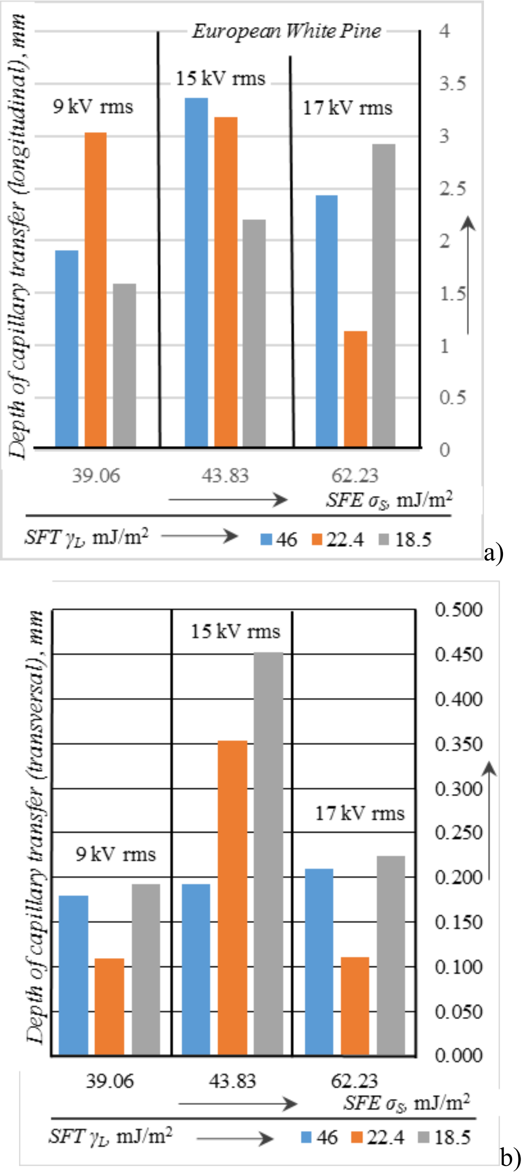

**Figure 5.** Effect of *APP*- treatment mode (voltage) - 9, 13 and 17 kV rms (50 Hz; air gap of 6 mm), used impregnating *FR*- solutions and consumption rate (maximum rate: 1.5 cm$^3$ per sample or 0.139 dm$^3$/m$^2$) on the depth of capillary transfer: longitudinal - capillary displacement (***a***) and transversal – wicking through the capillary walls (***b***) to the wood capillary direction.

The reduction in *SFT* of the impregnating *FR*- solution from 46 to 18.5 mJ/m$^2$ determines a substantial increase of the penetration depth - from 0.193 to 0.452 mm - 2.34 times higher, Fig. 5b. This reduction in the *SFT* gives a reduction in the depth of penetration with capillary displacement from 3.368 to 2.201 mm - 1.5 times less, Fig. 5a.

Usually this effective mode (15 kV rms) of plasma and surfactant enhanced capillary impregnation has a polar part of the *SFE* that is equal to and greater than the dispersive part of the *SFE*, Table 2, Fig. 3.

The transition towards a more intensive mode of *APP*-activation (17 kV rms), Fig. 2, does not give a positive result in spite of the increased *SFE* and its polar part, and the *PS*-efficiency parameter, Table 1 and 2, Fig. 4.

## CONCLUSION

The plasma and surfactant enhanced impregnation process has been determined primarily via the wicking through the capillary walls and not via the capillary action. That is why we use the term surface impregnation instead of capillary impregnation.

There are two types of surface impregnation:

- *first*, the capillary impregnation which is a result of capillary action and
- *second*, the penetration or wicking through the capillary walls.

The process of penetration through the capillary walls (wicking) is essential for the effectiveness of the surface impregnation because the process of capillary action and displacement refers to a much smaller part of the wood sample surface.

The obtained experimental results show that the General rule of the penetration-spreading process efficiency parameter: *PS* > 0, is true and applicable for both of the studied cases – the capillary impregnation and the wicking impregnation.

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