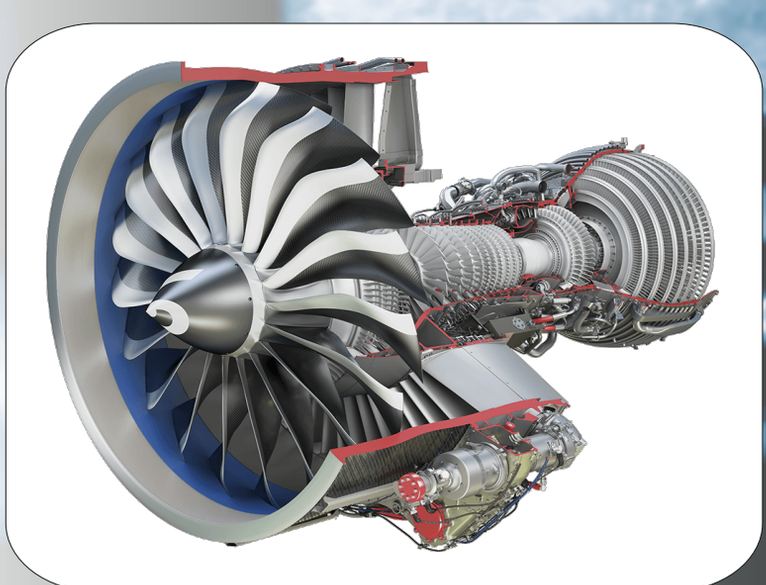
International journal
for science, technics and
innovations for the industry

MACHINES TECHNOLOGIES MATERIALS

YEAR X Issue 1 / 2016 ISSN 1313-0226



Published by
Scientific technical
Union of Mechanical Engineering

MACHINES, TECHNOLOGIES, MATERIALS

INTERNATIONAL JOURNAL

PUBLISHER

SCIENTIFIC TECHNICAL UNION OF MECHANICAL ENGINEERING

108, Rakovski Str., 1000 Sofia, Bulgaria
tel. (+359 2) 987 72 90,
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journal@mech-ing.com,
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ISSN 1313-0226
YEAR IX, ISSUE 1 / 2016

The current issue and the first issue of  journal and the conditions for publication can be find on
www.mech-ing.com/journal

C O N T E N T S

CAPILLARY PENETRATION (SPREADING AND WICKING) MECHANISMS IN PLASMA-AIDED SURFACE FINISHING PROCESSES

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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 surface finishing process of capillary impregnation with nitrogen- and phosphorous flame retardant containing water solution. The surface pre-treatment in atmospheric pressure dielectric barrier discharge plasma substantially alters its capillary activity – the spreading on the wood surface and the wicking in the depth of wood, thus improving some basic characteristics of the impregnation process. This study has been developed as part of a large investigation on plasma-chemically activated (polarized, functionalized) wood surface and surfactants enhanced plasma aided capillary impregnation with nitrogen- and phosphor flame retardant containing water solution. The experimental studies of capillary activity changes on European white pine (Pinus Sylvestris, Bulgaria) wood surfaces using selected surfactants and spreaders show that they have substantial contribution to the effective plasma-aided capillary activity and impregnation processes.*

Keywords: ATMOSPHERIC DIELECTRIC BARRIER DISCHARGE, CONTACT ANGLE MEASUREMENT, FLAME RETARDANT, PLASMA-AIDED CAPILLARY IMPREGNATION, SESSILE DROP TECHNIQUE, SURFACE ENERGY DETERMINATION.

1. Introduction

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 achieved by using a new *plasma-aided surface finishing process* of capillary impregnation. This *plasma-aided technology* comprises a surface plasma-chemical pre-treatment for alteration of chemical activity of wood surface as well as its electrical (ionic) and *capillary activities*, and in general for improvement of the *capillary impregnation process*, [1].

A technological system of plasma device and applicators has been created to produce cold technological plasma out of technological line or "*in situ*" through *air dielectric barrier discharge* (*DBD*) at atmospheric pressure and room temperature. The cold plasma pre-treatment of wood improves water solution spreading and wicking speed as well as a specific amount of the adsorbed flame retardant trough wood surface. In this way, the plasma pre-treatment of wood and wooden products improves its flame retardation [1, 2 and 6].

The objective of this paper was to study the effect of plasma pre-treatment on *European white* or *Scots pine* (*Pinus Sylvestris*, Bulgaria) wood surface functionalization as well as the effect of wood surface polarity on the wetting phenomena, both aiming to improve the capillary impregnation process. This study has been developed as part of a large research on plasma-chemically activated wood surface and flame retarded constructive wood.

2. Experimental Investigation

Wetting phenomena of wood may be characterized by using thermodynamic wetting parameters, for example contact angles, surface free energy, and work of adhesion, work of spreading or work of wetting, [3].

The wetting phenomena on a real (non-ideal) - *rough*, *porous*, *heterogeneous*, or *hygroscopic* wood surface, Fig. 1, can be involved by: *i* - *spreading* of liquid over a solid surface; *ii* - *wicking* of a liquid into a porous solid such as wood.

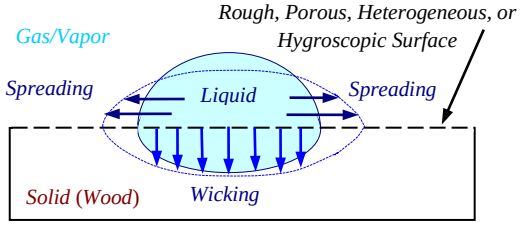

Fig. 1. *Young-Bikerman-Good model of wetting phenomena - the wetting phenomena on a real surface can be involved by: i - spreading of liquid over a solid surface; ii - wicking of a liquid into a porous solid such as wood.*

Wetting does not include dissolution or swelling of the solid by the liquid or any kind of chemical reaction between the materials that changes the system composition, (*Berg*, 1993).

Basic relations of wetting phenomena

Neumann and *Good* (1979) reviewed the classical techniques for measuring contact angles. Using well defined liquid, if the contact angle can be measured on a solid surface, the work of adhesion can be determined and the solid surface can be revealed. The most widely used technique, also regarding wood, involves digital image analysis of the profile dimensions of a droplet deposited on a horizontal surface from which the contact angle can be calculated - referred to here as the sessile drop method.

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.

It must be emphasized that the contact angle of a liquid as it advances slowly over a non-ideal surface (e.g. not chemically homogeneous, porous and not perfectly smooth, as in the case of wood surfaces) changes (decreases) synchronously to droplet change and movement. 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.

Contact angle measurement

The *Sessile Drop Technique* is a method for the characterization of wood (solid) surface energy. The main premise of the method is that by placing a droplet of probe liquid with a known surface energy on the solid surface. The measured contact angle and the known surface energy of the probe liquids are the parameters which can be used to calculate the surface energy of a solid sample, [5].

The apparatus used for this study was a KRÜSS Drop Shape Analyzer DSA 30. Measurement of the contact angle with three specified test liquids ensures maximum accuracy when determining the wood surface free energy. 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, [5].

The aim of this study was to verify possibility of determining the contact angle values of the plasma pre-treated wood surface and calculate the surface free energy and its components from the obtained contact angle values using *Zisman*, *Equation of state* (EOS), *Fowkes* and *Wu* theory and calculation method. All methods described there are integrated in the KRÜSS Drop Shape Analysis program DS A1, [5].

The determination of surface energy of *European white pine* (*EWP*) and its disperse and polar components was performed after contact angle measurement with three probe liquids: *Water* (bifunctional; $\theta = 70.2 \pm 0.1$ deg, total surface energy - 72.8 mN/m; dispersive component - 21.8 mN/m; polar component - 51 mN/m; acid component - 25.5 mN/m, and base component - 25.5 mN/m); *Ethylene glycol* (acidic, $\theta = 41 \pm 0.1$ deg, total surface energy - 47.5 mN/m, dispersive component - 29.3 mN/m; polar component - 18.2 mN/m; and *n-Hexadecane* (neutral, $\theta = 10.3 \pm 0.1$ deg, total surface energy - 27.6 mN/m, dispersive component - 27.6 mN/m; polar component - 0 mN/m).

Contact angle measurement and capillary impregnation

Time-depending change of contact angle θ of a liquid 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) was determined by contact angle measurements 2 and 24 hours after atmospheric *dielectric barrier discharge* (*DBD*) surface pre-treatment in air.

A possible option 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.

Gravimetric study of capillary impregnation by dipping

Fast ongoing processes of penetration (spreading and wicking), Fig. 1, may not always be examined by contact angle measurement technique. In this case the penetration study can be performed gravimetrically by dipping the test sample in impregnating solution. The test sample was immersed for 60 sec, drained for 60 sec and then weighed by laboratory balance (0.001 gr). This sample was dried at room temperature for 24 hours before being weighed again. Thus, the penetration was defined integrally by the weight of the absorbed solution and its corresponding dry matter (*flame retardant substance*).

Plasma-chemical surface pre-treatment

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 the test samples for 60 sec in a non-equilibrium cold plasma of atmospheric air dielectric barrier discharge (*DBD*) at industrial frequency (50 Hz) and 15 kV (*RMS*) or about 21 kV (*PV*) voltage.

European white pine (Pinus Sylvestris)

Pines are among the most commercially important tree species valued for their timber in general construction work throughout the world. Commercial pines are grown in plantations for timber that is denser, more resinous, and therefore more durable than spruce. Pine wood is widely used in high-value carpentry items such as furniture, window frames, paneling, floors and roofing.

European or Scots white pine (*Pinus Sylvestris*) is a species of pine that is native to Europe and Asia, ranging from Western Europe to eastern Siberia, south to the Caucasus Mountains and Anatolia, and north to well inside the Arctic Circle in Scandinavia.

European white pine properties: *Hard pine wood*: *Subgroup C* (Red Pines): Red Pine (*Pinus resinosa*, US); Austrian or European Black Pine (*Pinus nigra*, Europe); and *Scots* or *European White Pine* (*Pinus Sylvestris*, Europe); *Density* (average dried weight) - 550 kg/m^3; *Moisture content* (*MC*): 8÷12 %; *Specific gravity* (basic/12 % *MC*): 0.39/0.55; *Tree size*: 20÷35 m tall, 0.6÷1 m trunk diameter; *Shrinkage*: Radial: 5.2 %, Tangential: 8.3 %, Volumetric: 13.6 %, T/R Ratio: 1.6; *Janka hardness* (12 % *MC*): 2.420 kN; *Modulus of rupture* (*MOR*): 83.3 MPa; *Modulus of elasticity* (*MOE*): 10.08 GPa; *Crushing strength* (compression strength parallel to grain): 41.5 MPa, [

European white pine a major source of timber and lumber intended for building constructions. The behavior of wooden structures during fire gives rise to strong public interest. This is our main motive for undertaking serious and ongoing for years research on flame retardancy of European white pine (pine) by using plasma aided flame retardancy. The method went through a successful industrial approbation in the practice of "*Interiorprotect*" Ltd. (Bulgaria), funded within a project by the *National Science Fund* at the *Ministry of Education and Science* (2005÷2010). The disclosure of various aspects of the phenomenon of plasma-aided flame retardancy represents a serious scientific interest.

Hard wood penetration or wicking

Capillary liquid penetration (or wicking) in hardwoods, like e.g. *European white pine* is mainly restricted to the filling of vessels and the first cells of rays and very occasionally axial parenchyma and sclerenchyma, [4].

In most of the permeable hardwood species (e.g. beech) vessels will be filled deeper and penetration in axial parenchyma and sclerenchyma would be more noticeable. The filling of a vessel by capillary impregnation is strongly reduced if tyloses are present. Extractives appeared to have none or only a very minor influence on the capillary penetration. Surface preparation can have some influence on impregnation penetration because sanding reduces the number of open cell capillaries in which flame retardant water solution can flow, [4].

Results and discussion

Surface energy of European white pine

Since wood surfaces are porous, rough and not perfectly smooth, sessile drop method requires some type of video capture in order to measure the contact angle which changes as the droplet is absorbed. The *n-hexadecane* completely wets the substrate and $\theta \rightarrow 0$. Time-depending change of the contact angle θ of two probe liquids – *water and ethylene glycol* as well as its slowly advance over the non-ideal wood surface are presented in Fig. 1.

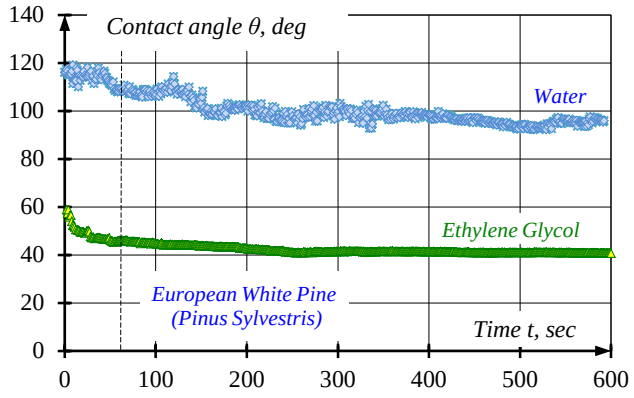

Fig. 2. *Time-depending change of the contact angle θ of probe liquids as well as its slowly advance over the non-ideal European white pine (Pinus Sylvestris) bare (non-plasma treated) wood surface.*

Based on the contact angle data of *EWP*-wood surface, the total surface free energy was obtained by using the *Zisman*, *Equation of state*, *Fowkes* and *Wu* theory and calculation methods, Table 1.

The polar and dispersive (non-polar) fractions are obtained using *Fowkes* and *Wu* theories. They are presented in Table 2.

Table 1. Calculated total surface free energy of *European White Pine* (*Pinus Sylvestris*) samples at about 22 ^{0}C.

Sessile Drop Test				
Total Surface Free Energy, mN/m				
Zisman Theory	Equation of State (EOS) Theory		Fowkes Theory	Wu Theory
28.40	22.71	± 7.95	29.06	29.86

The energy of the bulk part of a wood substrate is determined by the types of interactions that hold the substrate together. High energy substrates are held together by bonds, while low energy substrates are held together by forces. Covalent, ionic and metallic bonds are much stronger than forces such as Van der Waals and hydrogen bonding.

Table 2. Fractions of Total Surface Free Energy of *European White Pine* (*Pinus Sylvestris*) samples at about 22 ^{0}C.

Sessile Drop Test					
Fractions of Total Surface Free Energy					
Fowkes Theory			Wu Theory		
Polar Fraction	Disperse Fraction	Polarity/ Non-Polarity	Polar Fraction	Disperse Fraction	Polarity/ Non-Polarity
mN/m	mN/m	-	mN/m	mN/m	-
0.07	28.98	0.003/ 0.997	1.47	28.39	0.049/ 0.951

Low energy substrates such as *EWP-wood* (surface free energy: 29.6 mN/m) are wet harder than high energy substrates. The dispersive fraction of *EWP* surface energy is much greater than its polar fraction, Table 2, i.e. almost equal to the total surface free energy. In addition, more complete wetting (spreading and wicking) will occur if the substrate has a much higher surface energy than the liquid.

Wetting and capillary penetration of European white pine

The contact angle of a liquid as it advances slowly over a non-ideal surface decreases synchronously to droplet movement. The high resolution camera of KRÜSS Drop Shape Analyzer DSA 30 captures the image, which was analyzed by using image analysis software. By taking pictures incrementally as the droplet advances over the surface we get a good time-depending change of the contact angle, Fig. 3 and 4.

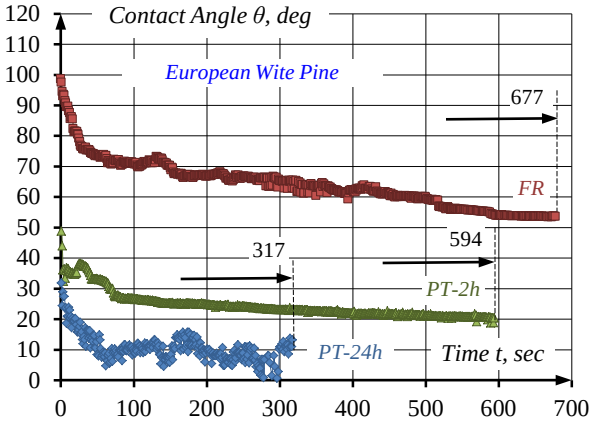

Fig. 3. Time-depending change of the contact angle θ of basic phosphor and nitrogen containing flame retardant as it advances slowly over the *European white pine (Pinus Sylvestris*) bare (non-plasma treated) sample surface (*FR*); 2 hours after plasma surface pre-treatment (*PT-2h*); and 24 hours after plasma surface pre-treatment (*PT-24h*).

This approach, however, is only applicable for slower running processes of wetting and capillary penetration, Fig. 3. In these cases the contact angle is very quickly reduced to zero and the software can not correctly implement image analysis. For rapid processes of capillary penetration only two parameters can be reported - initial contact angle (ICA) and time of penetration, Table 3.

Table 3. Sessile drop measurement with three test flame retardant (*FR*-) liquids for *European white pine* (*Pinus Sylvestris*) sample before and 2 hours/24 hours after plasma pre-treatment.

FR				
No	Samples	Age	Initial Contact Angle (*ICA*)	Time of penetration
		h	deg	sec
1.	Non-plasma treated	-	28.6	677
2.	Plasma treated	2	35.8	594
3.	Plasma treated	24	18.1	317
FR with 5 vol. % phosphor anionic surfactant (FR5)				
No	Samples	Age	Initial Contact Angle (*ICA*)	Time of penetration
		h	deg	sec
1.	Non-plasma treated	-	28.6	40
2.	Plasma treated	2	35.8	3
3.	Plasma treated	24	18.1	3
FR with 5 vol. % phosphor anionic surfactant and 0.1 vol. % siloxane surfactant (spreader) (FR5S)				
No	Samples	Age	Initial Contact Angle (*ICA*)	Time of penetration
		h	deg	sec
1.	Non-plasma treated	-	21.3	7
2.	Plasma treated	2	8.0	2
3.	Plasma treated	24	21.1	7

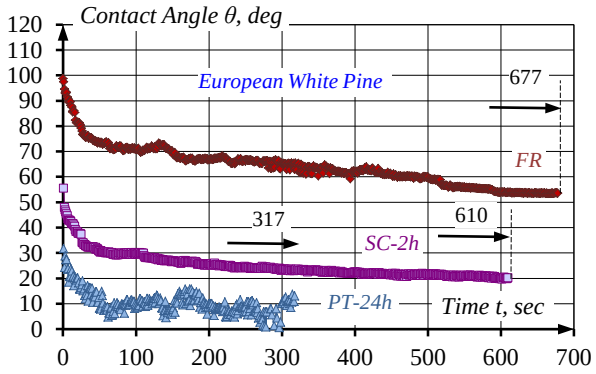

Fig. 4. Time-depending change of contact angle θ of basic phosphor and nitrogen containing flame retardant as its advance slowly over the *European white pine (Pinus Sylvestris)* bare (non-plasma treated) sample (*FR*); 2 hours active depolarization after plasma surface pre-treatment (*SC-2h*); and 24 hours after plasma surface pre-treatment (*PT-24h*).

The obtained results confirm the possibility to use "*open time*" up to 24 hours for capillary impregnation using flame retardant water solution with surfactants (*FR5* and *FR5S*), Table 3.

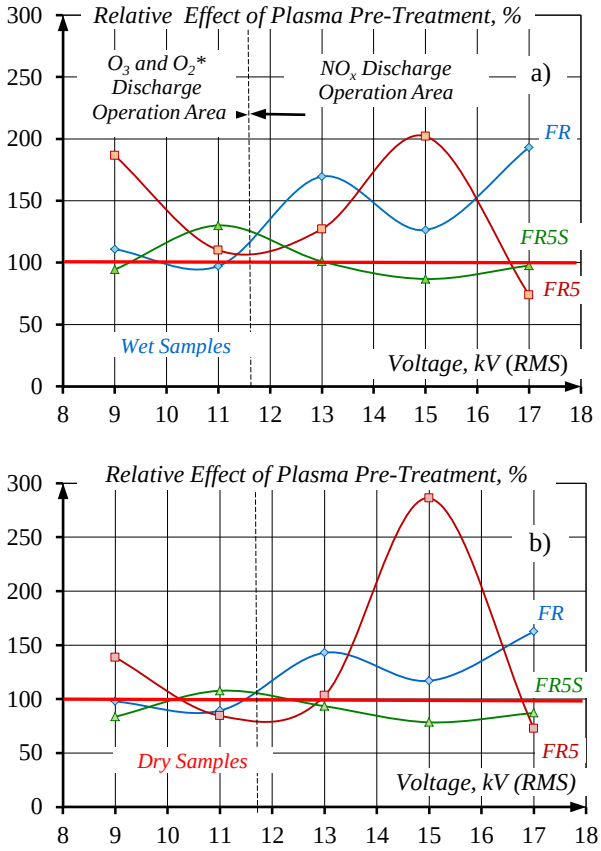

Fig. 5. Voltage-depending change of the relative effect of plasma-aided capillary impregnation – increase compared to the classic capillary impregnation, with three flame retardant water solution (30 mass % dry substances): *FR* – basic phosphor and nitrogen flame retardant containing water solution; *FR5* – *FR*-solution with 5 vol. % phosphor anionic surfactant; *FR5S* – *FR5*-solution with 0.1 vol. % siloxane surfactant (spreader): a – relative effect of penetrated solution (wet sample); b – relative effect of penetrated dry substance (flame retardant). Weight increasing for classic capillary impregnation (100 %): for the *FR*-solution: wet – 9.80 %; dry – 4.01 %; for *FR5*-solution: wet – 10.86 %; dry – 4.02 %; and for the *FR5S*-solution: wet – 14.44 %; dry – 5.24 %.

Besides the registered significantly less time for capillary penetration a hypothesis was experimentally verified for larger quantity of *FR*-solution and active substance when using *FR*-solution with surfactants (FR5 and FR5S).

It is experimentally verified that there are modes of plasma pre-treatment, which provide more absorbed solution, Fig. 5a, and more absorbed dry matter, Fig. 5b.

The hypothesis of electric polarization of wood samples at room temperature during plasma pre-treatment (plasma electret) is also experimentally verified. For this purpose after plasma pre-treatment the wood samples are being placed in depolarization conditions by wrapping them in aluminum foil, Fig. 6.

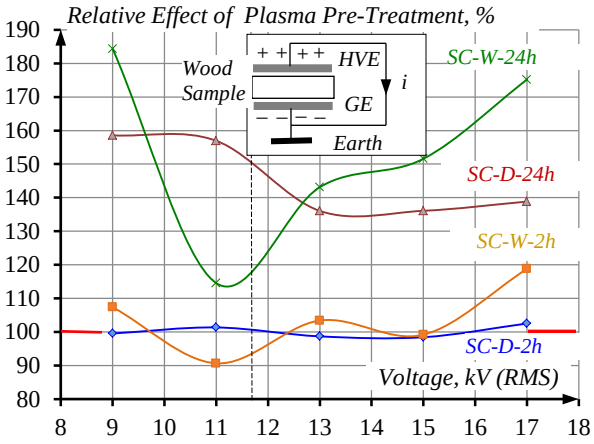

Fig. 6. Voltage-depending change of the relative effect of plasma-aided capillary impregnation in wet (*-W-*) and dry (*-D-*) state – increase compared to the classic capillary impregnation, with basic flame retardant (*FR*) water solution (30 mass % dry substances). The impregnation was carried out after 2 and 24 hours of effective depolarization. *HVE* – high voltage electrode; *GE* – ground electrode; *i* – short circuit current. Weight increasing for classic capillary impregnation (100 %) with basic *FR*-solution: wet – 9.80 %; dry – 4.01 %.

It is established that after two hours of depolarization at room temperature there is no change in the contact angle, Fig. 4 and 3, the relatively positive (compared to non-plasma treated sample) effect, both in wet and in dry conditions, is preserved. This show that there is no effective depolarization of the plasma pre-treated samples, which may be explained by the preservation of the dipole polarization (hetero-discharge) and the polarization resulting from created on the surface radicals.

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