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THE SURFACE DENSITY OF THE POWER AS A BASIC PARAMETER OF THE PLASMA-CHEMICAL MODIFICATION OF MATERIALS IN A BARRIER ELECTRICAL DISCHARGE

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Abstract. The realization of plasma-chemical processes for surface modification of polymer materials at normal atmospheric pressure is mainly defined by the active electric power of the corona or barrier electric discharge related to a unit area of the treated surface or by the surface density of the active power. This basic parameter of the plasma-chemical modification of materials can be determined experimentally or through the static volt-ampere characteristic.

Key words: barrier electric discharge, plasma-chemical modification of materials, surface density of active power.

INTRODUCTION

The technology of plasma-chemical surface modification that can change purposefully the surface properties of polymers and polymer materials finds successful application in the plastics and textile industry. In recent years a lot has been done for the development of plasma surface modification technology by revealing new opportunities for modifying the surfaces and their properties: adhesion, hydrophilicity, bio-compatibility, protective coating, friction and wear, composites and thin-film [1, 2].

The surface plasma-chemical technology that uses the barrier (capacity) electric discharge at atmospheric (high) pressure is a good alternative of vacuum-plasma technologies for modification with **DC** glow or **RF** (**R**adio- or **H**igh-**F**requency) discharges. The realization of plasma-chemical processes in the course of the modification of a polymer surface should depend on the surface density of the active power. Determining this electric parameter of the technological process based on the static volt-ampere characteristic of the discharge, on one hand, and its impact upon the plasma-chemical modification of materials, on the other hand, permits the realization of a new approach to the controll of this process.

The task of the present work is to propose and substantiate a methodology of determining the effectiveness of plasma-chemical modification based on the introduction of the surface density of the active power as a basic parameter of the electric discharge.

The experimental technological investigation of the process of plasma-chemical modification at atmospheric pressure is performed on non-woven textile filter (high-porous) media of the *"Geotextile 500"* type (*Non-Woven Textile* Ltd., Sofia, Bulgaria), based on **PET** (polyethylene terephtalate).

THEORETICAL AND EXPERIMENTAL DETERMINATION OF THE SURFACE DENSITY OF THE ACTIVE POWER

Static volt-ampere characteristic

The static volt-ampere characteristic for the *average value of the current* $I_{moy} = \varphi (U_{eff})$ is in the foundations of the created concept for the effectiveness of the plasma-chemical treatment of polymers and polymer materials [3].

The investigations performed by Tsuda - Sato - Tahara (1954) and Filipov - Emelyanov (1958) demonstrate that the volt-ampere characteristic of the barrier (capacity) discharge for the average value of the current consists of two straight lines crossing each other at the so called *critical voltage* U_{cr} :
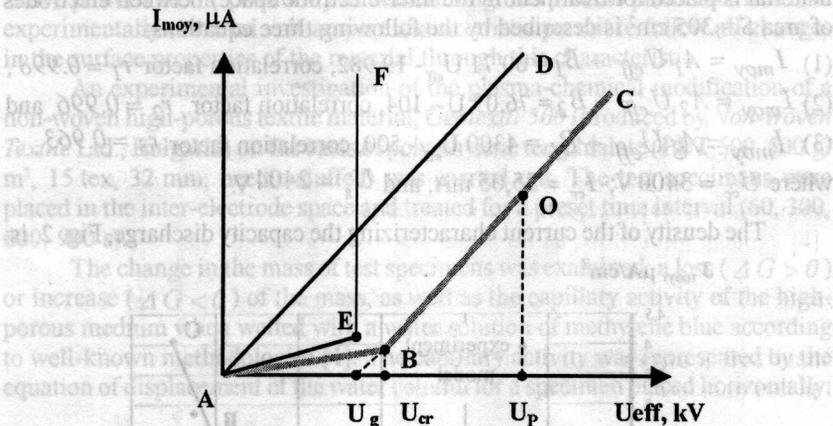

Fig. 1. Static volt-ampere characteristic of a technological capacity discharge (ABC), voltage drop across the barrier (AD) and voltage drop on the discharge (technological) gap (AEF).

• at voltages $U_{eff} \leq \sqrt{2}\, U_{cr} : I_{moy} = \dfrac{2}{\pi} U_{eff}\, C_\Sigma\, \omega$, while at $U_{eff} = 0$:

$I_{moy} = 0$, i. e. the straight line passes through the origin of the coordinate system;
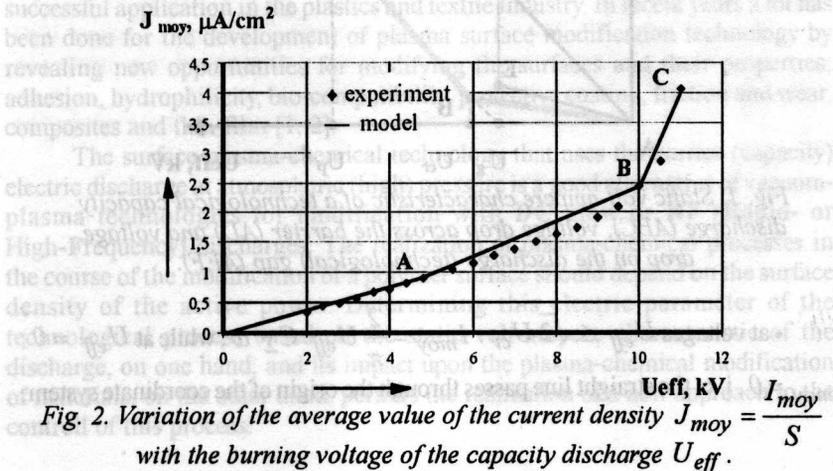
• at voltages $U_{eff} \geq \sqrt{2}\, U_{cr}: I_{moy} = \dfrac{2}{\pi}\left(U_{eff} - U_g\right)C_b\,\omega$, while at $U_{eff} = U_g: I_{moy} = 0$, and at the so called *critical point* $C: U_{eff} = U_{cr}$, $I_{moy} = I_{cr}$ as shown in Fig. 1.

It is known that *chemically active ions* ($O_2^+, O_2^-, O^+, O^-, N_2^+, N_2^-, N^+, N^-$ for the air) and *electrons* are obtained as a result of the gas *ionization*, whereupon the magnitude of the average value of the current depends on the intensity of the ionization process and is its integral characteristic. The intensity of the plasma-chemical conversion depends on the quantity of chemically active particles (ions and electrons), i. e. the mass of the destroyed (through degradation by the generated volatile product) or of the synthesized (by cross-linking) substance per unit of time and per unit of area will be proportional to the average value of the current density on the treated surface: $J_{moy} = I_{moy}/S$.

The experimental verification of the validity of the volt-ampere characteristic, presented above for the average value of the current, indicates that the electric characteristic can be modeled by the mentioned system of three crossing straight lines indeed. The electrical discharge in *idle mode* (when no material is placed for treatment in the inter-electrode space) between electrodes of area $S = 305$ cm^2 is described by the following three equations:

(1) $I_{moy} = A_1 U_{eff} + B_1 = 60.71\, U_{eff} - 19.982$, correlation factor $r_1 = 0.998$,

(2) $I_{moy} = A_2 U_{eff} + B_2 = 76.07\, U - 104$, correlation factor $r_2 = 0.996$ and

(3) $I_{moy} = A_3 U_{eff} + B_3 = 4300\, U_{eff} - 500$, correlation factor $r_3 = 0.963$,

where $U_{cr} = 3400$ V; $I_{cr} = 55{,}05$ mA, and $U_g = 2404$ V.

The density of the current characterizing the capacity discharge, Fig. 2, is:

Fig. 2. Variation of the average value of the current density $J_{moy} = \dfrac{I_{moy}}{S}$ with the burning voltage of the capacity discharge U_{eff}.

(3) $\quad J_{moy} = (A/S)U_{eff} + (B/S) = A\,U_{eff} + B$, mA/cm² at $U_{eff} > 3400$ V.

Surface density of the active power

The active power P_a of the capacity electric discharge can be determined through the parameters of the static volt-ampere characteristic:

(4) $\qquad P_a = U_{eff}\left(I_{moy} - I_{cr}\right)$ at $U_{eff} > U_{cr}$, W,

and the surface density of the active power P_a is:

(5) $\qquad p_a = \dfrac{P_a}{S} = U_{eff}\left(J_{moy} - J_{cr}\right) = U_{eff}\left(J_{moy} - 0{,}0018\right)$, W/m².

EXPERIMENTAL INVESTIGATION
OF THE PLASMA-CHEMICAL MODIFICATION
OF HIGH-POROUS POLYMER MATERIALS

The theoretically substantiated thesis about the connection between the effectiveness of the plasma-chemical modification and the surface density of the active power and the possibility of determining this process parameter from the experimentally obtained volt-ampere characteristic permit to follow all changes in the surface properties of the material through this characteristic.

An experimental investigation of the plasma-chemical modification of a non-woven high-porous textile material, *Geotextil 500* (produced by *Non-Woven Textile* Ltd., Bulgaria) on the basis of polyethylene terephtalate (**PET** 500, 500 g/m², 15 tex, 32 mm, needle-stuffed) was carried out. The test specimens were placed in the inter-electrode space and treated for a preset time interval (60, 300, 600, 900 s).

The change in the mass of test specimens was examined: a loss ($\Delta G > 0$) or increase ($\Delta G < 0$) of the mass, as well as the capillary activity of the high-porous medium when wetted with a water solution of methylene blue according to well-known methodologies [1]. The capillary activity was represented by the equation of displacement of the water column for a specimen placed horizontally:

(6) $\qquad H^2 = A\,t + B$,

where H is the displacement of the water column in mm; A - the speed of capillary displacement in mm²/s; and B the initial displacement of the water column in relationship with wetting of the polymer surface by the solution in mm².
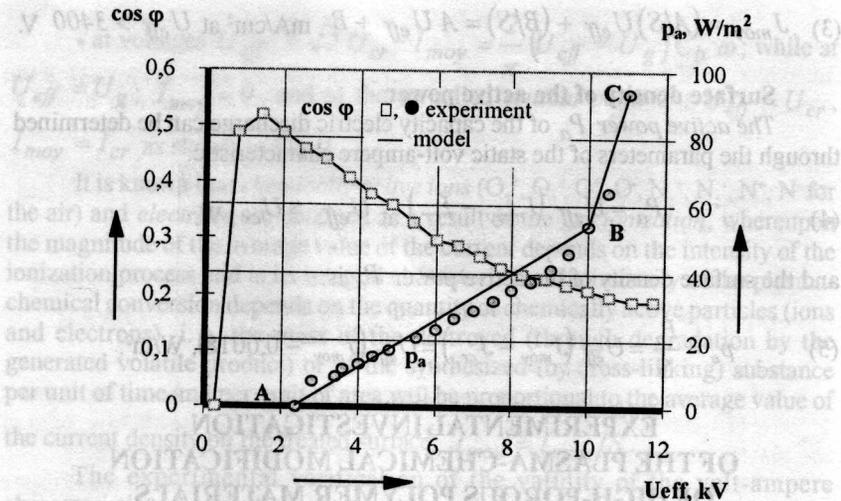
Fig. 3. Relationships between the surface density of the active power $p_a = \dfrac{P_a}{S}$ and of the power factor $\cos\varphi$, on one hand, and the burning voltage of the capacity discharge, U_{eff}, on the other hand.
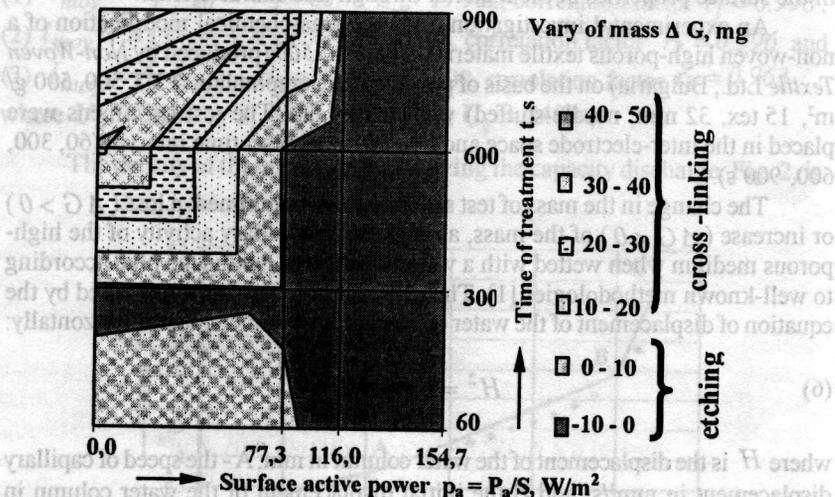

Fig. 4. Variation of the mass ΔG of specimens from non-woven high-porous textile materials in relationship with the surface density of the active power p_a and the duration of plasma treatment t.

The relative change in the mass of test specimens shows something very interesting: the mass was not reduced because only of etching (a physical process) or of emitting a volatile product generated by degradation (a chemical process), but was actually increased, which can be explained solely with cross-links on the polymer surface through the reactions between the active species from the oxygen-containing plasma and surface atoms. This is related to an air capacity discharge, which involves the generation in the discharge of molecules of excited oxygen as a result of the decomposition of the ozone generated before that [3].
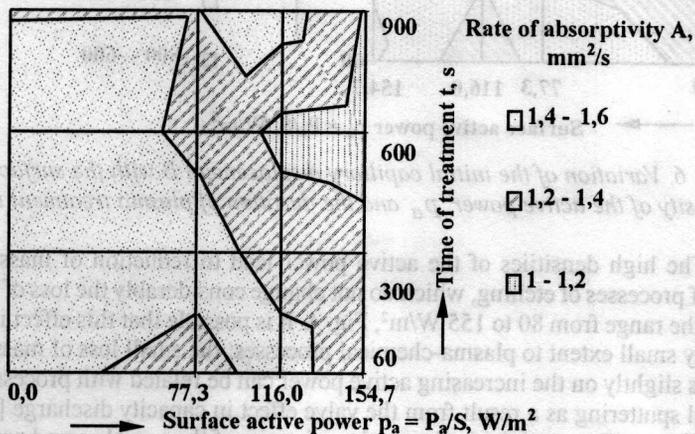

Rate of absorptivity A,
mm²/s

☐ 1,4 - 1,6

☐ 1,2 - 1,4

☐ 1 - 1,2

Fig. 5. Variation of the speed of capillary displacement A with the surface density of the active power p_a and the duration of plasma treatment t.

Most probable is the generation of ozone with the participation of molecular ions (O_2^+, O_2^-), i. e. this is the case at low densities of the active power. The dissociation of the oxygen molecule creates conditions for absorbing the ozone already generated, and after some dynamic equilibrium the ozone quantity is reduced.

In such a way, at low surface density of the active power: up to 80 W/m², processes of cross-linking are dominated in the oxygen-containing plasma of the barrier discharge. A maximum effect of increasing the mass was observed at minimum densities of the active power and large time intervals of diffusion - 10 to 12 min.
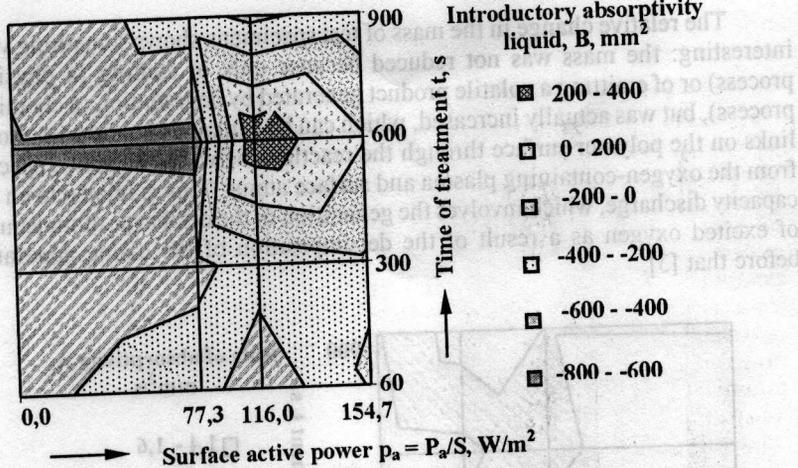
Fig. 6. Variation of the initial capillary displacement B with the surface density of the active power p_a and the duration of plasma treatment t.

The high densitiies of the active power lead to reduction of mass as a result of processes of etching, which do not change considerably the loss of mass within the range from 80 to 155 W/m^2, Fig. 4. It is possible that this effect is due in a very small extent to plasma-chemical processes; the small loss of mass that depends slightly on the increasing active power can be related with processes of physical sputtering as a result from the valve effect in capacity discharge [3].

The capillary activity indicates the existence of the two observed areas of specific plasma-chemical modification, Figs. 5 and 6. The initial capillary displacement W is large in the area of etching, while it takes on negative values in the area of cross-linking, Fig. 6.

CONCLUSION

The surface density of the active power allows outlining of specific areas of plasma modification, but the multiple chemical processes effected concurrently do not permit the manifestation of a direct relationship between the surface density of the active power and the degree of etching or cross-linking.

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