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# SURFACE TREATMENT OF POLYMER MATERIAL USING ARGON GLOW DISCHARGE

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Surface treatment of polymer material (thin polyester samples) was performed in the DC glow discharge, using Ar gas. The effect of the experimental parameters of the glow discharge (the gas pressure and the sample treatment time) on the wettability of the samples was studied. The wettability was characterized by the water repellency (water spray test). In the present work, it was shown that at a constant gas pressure (270 or 670 Pa), the wettability of the polyester sample was decreased by increasing the exposure time of the sample in the glow discharge. At constant exposure times (2, 5, 10 or 15 min) the wettability of the polyester sample was increased by increasing the gas pressure. This is due to the formation of hydrophilic groups, which increased by increasing the density of electrons and/or metastables.

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## 1. Introduction

The plasma treatment of surfaces in which plasma active species interact only very superficially with the material, i.e. with the adsorbed surface monolayers or with the first few monolayers of the surface material itself, is considered. Such interaction can significantly affect the surface energy, wettability, printability, adhesion and other important properties of surface [1]. This sort of plasma treatment is called "surface activation" [2].

Using cold plasmas for surface activation of polymers is not a new subject. It was first suggested by Beauchamp and Buttrill [2] in 1968. It is generally difficult to adhesively bond polymers to themselves or other materials. Polymers such as fluoropolymers, which are characterized by high chemical inertness, thermal stability and electrical insulating properties, have very low surface tension, which consequently cause negligible bonding to the other materials, especially metals [3]. Plasma surface treatment allows modification of the surface characteristics of polymers and improves their bonding to other materials, without affecting the bulk properties. The methods employed to modify properties of polymeric surfaces include surface activation, deposition and grafting. Surface activation is especially important for polymeric materials.

Exposure of polymers to suitable plasmas can cause chemical and physical changes to their surface or near-surface layers. These changes produce more reactive surfaces and affect wetting properties, cross-linking and molecular weight [4]. Surfaces can thus be engineered to achieve the necessary properties, such as wettability, adhesion, barrier protection, material selectivity and even biocompatibility. The polymer surface is thus modified by the reactive species generated in the glow discharge [5].

The polyester treatment is interpreted assuming two steps for the reaction processes: in the first step, chemical bonds are broken by energy transfer from reactive particles to the surface, and in the second step, new chemical bonds are generated between atoms produced in the plasma or from resulting dissociation processes near the polymer surface [6].

The aim of the present work is to investigate the surface treatment of polymer material (polyester samples) using DC glow discharge, in order to change and/or modify the wettability of thin polyester layers. The effect of the experimental parameters, the gas pressure $P$ and the duration of exposure $t$ on the wettability of thin polyester layers are studied and discussed.

## 2. Experimental setup

Plasma treatments were carried out in a Pyrex glass tube of 15 cm diameter and 30 cm long. Two electrodes made of Al disks of diameter 10 cm were placed inside the discharge tube. By means of rotary and diffusion pumps, the discharge chamber was evacuated down to about $10^{-3}$ Pa ($10^{-5}$ Torr, 1 Torr = 133.3 Pa). During all measurements, a continuos flow of a gas through the discharge chamber was maintained. Noble feed gases such as Ar, N, He, $O_2$ are used since they tend to initiate cleavage without grafting to the surface. High purity Ar gas (99.9 %) was used as the working gas and was fed to the chamber through a needle valve. The pressure of the working gas was varied between $13 - 670$ Pa and measured using a digital vacuum gauge (VAP 5). The discharge chamber was operated using 1000 VDC power supply, whereas the current density was varied between $2 - 15$ mA/m$^2$. Figure 1 shows a schematic drawing of the apparatus used in this study.

In the present work, the surface treatment, using argon plasma, was performed with polyester layers in order to change their wettability. The use of Ar certainly favourizes the crosslinking of the polyester in order to achieve stabilization of the

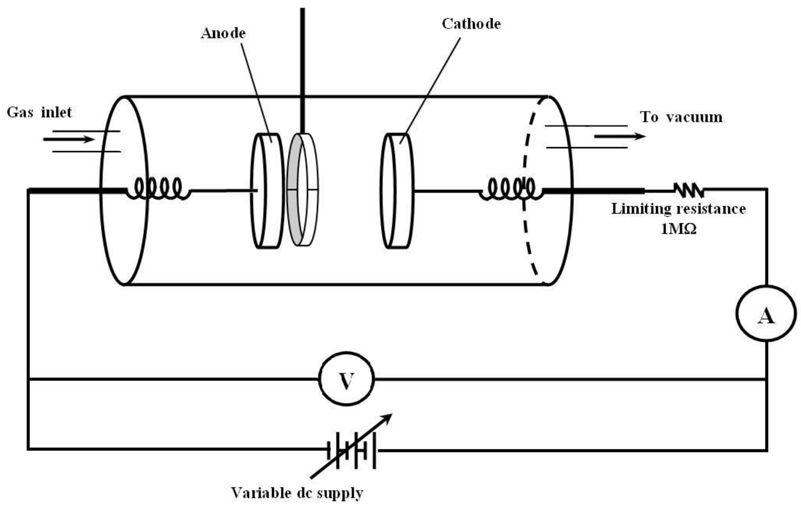


*Fig. 1. A schematic drawing of the apparatus used for this study.*

plasma treatment [7]. Also, the argon gas has a lower dielectric breakdown voltage. The shapes of polyester samples was circular, each of them of a diameter of 20 cm and thickness of 0.1 cm. The polyester sample was introduced into the discharge chamber using a small holder placed in front of the anode surface. The samples are cut to the shape and size of the anode electrode and cleaned with aceton to remove dirt and additives prior to plasma treatment. The experimental parameters considered in this treatment are the gas pressure ($P$) and the treatment exposure time ($t$). The discharge current and the interelectrode distance were fixed at 5 mA and 4 cm, respectively, while the discharge voltage was varied between 540 to 680 V. The wettability of the polyester layers was determined before and after the plasma treatment using the "the water repellency test". This test measures the percentage of free water and the state of dampness of water-proof textiles. Through a nozzle (19 small holes of diameter 0.889 cm), 250 ml of distilled water (at room temperature) was sprayed from a pot to a test specimen laid sloping at an angle of 45° (for $25 - 30$ sec), then the percentage of free water clinging to the specimen was measured. In the present work, the treatment exposure time was varied in the range of $2 - 15$ minutes and the gas pressure was varied in the range of $13 - 670$ Pa, while the discharge current is kept at 5 mA in all measurements.

## *3. Results and discussion*

Figures 2 and 3 show the water repellency which decreased from 70 % at 270 Pa gas pressure to 52 % at 670 Pa after 2 minute exposure time in plasma. By increasing the exposure time to 15 minutes, the water repellency increased up to 80 % at 270 Pa and to 70 % at 670 Pa. This means that the wettability of the polyester layers decreased by increasing the treatment exposure time. These figures

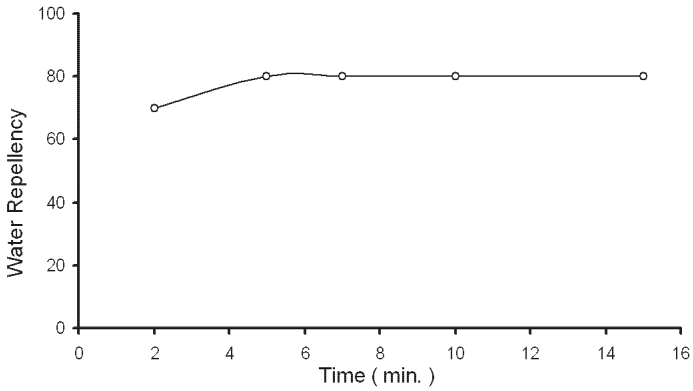


*Fig. 2. The relation between the water repellency as a function of the treatment exposure time at a constant gas pressure ($P = 270$ Pa) and at discharge current of 5* mA.

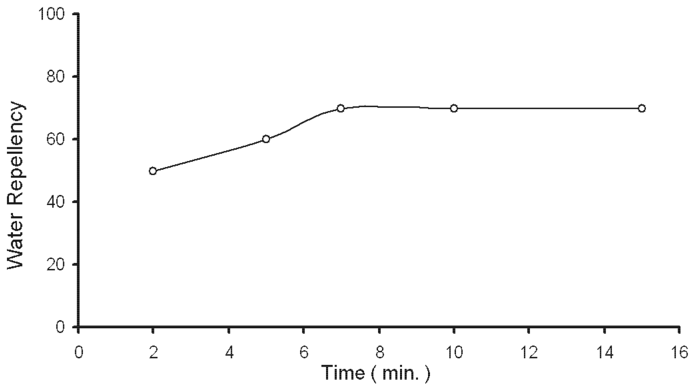


*Fig. 3. The relation between the water repellency as a function of the treatment exposure time at a constant gas pressure ($P = 670$ Pa) and at discharge current of 5* mA.

also show that the change in the water repellency is large at short exposure times and it becomes very small with increasing the exposure time. In plasma surface treatments using glow discharge, the maximum treatment efficiency is reached in very short exposure times [5].

On the other hand, Figs. 4 − 7 show the water repellency of the polyester layers as a function of the gas pressure, at constant exposure times of 2, 5, 10 and 15 min, respectively. The repellency of the polyester layers decreased by increasing the gas pressure. Thus, the wettability of the polyester layers increased by increasing the gas pressure. When the gas pressure was increased, the number of collisions between the charged particles and the neutral atoms increased inside the discharge tube, leading to an increase of the electron density. These electrons lose more of their energy in the collisions, so, the electron temperature decreased, i.e., increasing the

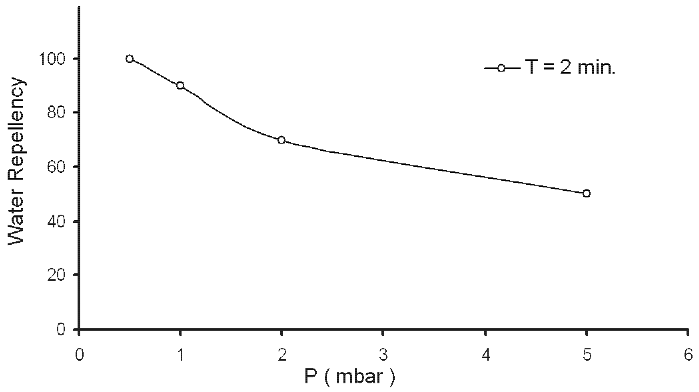


*Fig. 4. The relation between the water repellency as a function of the gas pressure at a constant treatment duration time of 2* min *and discharge current of 5* mA.

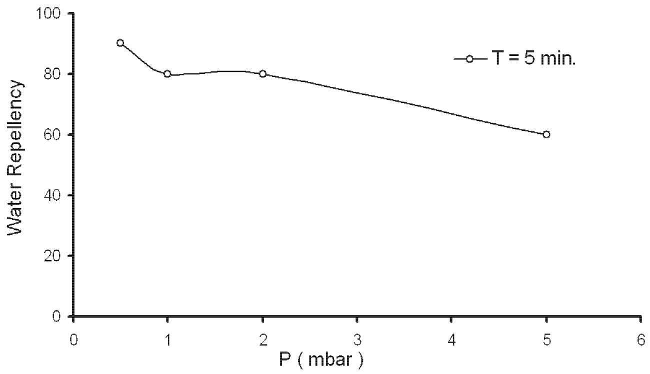


*Fig. 5. The relation between the water repellency as a function of the gas pressure at a constant treatment duration time of 5* min *and discharge current of 5* mA.

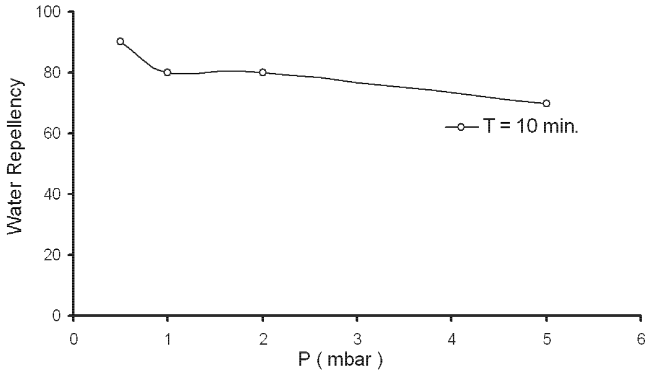


*Fig. 6. The relation between the water repellency as a function of the gas pressure at a constant treatment duration time of = 10* min *and discharge current of 5* mA.

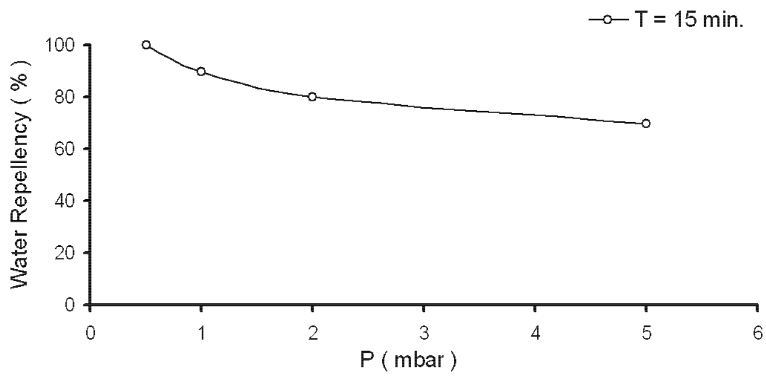


*Fig. 7. The relation between the water repellency as a function of the gas pressure at a constant treatment duration time of 15* min *and discharge current equal to 5* mA.

gas pressure increases the electron density and decreases the electron temperature at the same time. The best plasma surface treatment of polymers is obtained with high plasma density and low energy of electrons or ions [1, 8], so, the wettability of the polyester samples increased by increasing the gas pressure.

The experimental data for the polyester wettability agree with the results, obtained by Clement et al. [8]. They studied the wettability of polystyrene thin films using DC pulsed glow discharges in nitrogen gas. They showed that the metastable atoms of nitrogen gas seem to play an important role for the surface treatment. It is generally admitted that the chemical and physical nature of the outer monolayers of the polymer are modified by the electronically, vibrationally and rotationally excited species produced in the plasma.

In the present work, the polyester layers are put on the anode surface to be bombarded by the electrons, which move from the cathode to reach the anode. The bombardment of the polymeric surfaces with the energetic particles breaks the covalent bonds on the surface of the bombarded polymer and leads to the formation of surface radicals on the treated polymer. These surface radicals, in turn, react with the active species of the plasma to form various active chemical functional groups on the surface. These groups react strongly with the hydrogen in water. This property is the so called hydrophilic property [3]. Formation of the hydrophilic groups increased by increasing the number of electrons which have low energy. So, the wettability of polyester samples increased by increasing the gas pressure, because increasing the gas pressure increases the number of electrons and decreases their energy. Surface contaminants and weakly-bounded polymer layers can dissociate into volatile by-products that are removed by pumping from the discharge tube. Grill [3] reported that plasma treatment exposures for a few to a few tens of minutes can make hydrophilic the surfaces of most polymers, including polyolefines, polyesters, polyamides and fluoropolymers. The active plasma species attack the polymer. Mahlberg et al. [9] have shown that the substrate surfaces became highly hydrophilic when exposed for 5 min, or longer to the plasma. On the other hand, Clement et al. [10] stated in that in DC pulsed conditions, the chemical effects are the main source of the increase in hydrophilicity which is realized by the formation of polar functions. According to experimental conditions, the discharge may modify chemically and physically the polymer surface. Thus the increase of polystyrene wettability is mainly due to the formation of polar functions which are of great interest to improve surfaces and cause the incorporation of hydrophilic groups, such as carbonyl, carboxyl, hydroxyl and amino groups, into the surface of the polymers. Polar functions orient themselves toward the polymer bulk and may interact with other to form hydrogen bonds, which establish physical linkages within the surface and its stabilization.

## 4. Conclusion

Surface treatment of polymer material (industrial polyester sample) was performed in the DC glow discharge, using Ar gas. It is concluded that at a constant gas pressures, the wettability of the polyester samples decreased by increasing the exposure time in the glow discharge. At constant exposure time, the wettability of the polyester sample increased by increasing the gas pressure.

Species with long lifetime and created in the glow discharge have an important role in the surface modification. Thus it is necessary to analyze the plasma reactive particles and the polymer surface to characterize the plasma surface interaction. XPS must be done to detect the chemical surface changes on the samples. In general, plasma treatments lead to the appearance of a shoulder at higher binding energies, which was taken as an indication of the buildup of oxygenated carbon centers.

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## POVRŠINSKA OBRADA POLIMERA U TINJAVOM ARGONSKOM IZBOJU

Površinski smo obrađivali polimerni materijal (tanke uzorke poliestera) u istosmjernom tinjavom argonskom izboju. Proučavali smo učinke eksperimentalnih parametara izboja (tlaka plina i vremena izlaganja u izboju) na močivost uzoraka. Močivost smo određivali mjerenjem odbojnosti vode (metoda prskanjem vode). U ovom se radu pokazuje da se na stalnom tlaku plina (270 ili 670 Pa), močivost uzoraka poliestera smanjuje za dulja vremena izlaganja u izboju. Za određena vremena izlaganja (2, 5, 10 ili 15 min), močivost uzoraka je porasla pri povećanom tlaku argona. Razlog tome je stvaranje hidrofilnih grupa koje su bile brojnije pri povećanoj gustoći elektrona i/ili metastabila.