

CORRELATION BETWEEN SURFACE MODIFICATIONS INDUCED ON PET/TiO₂ SAMPLE BY DBD PLASMA PRODUCED IN He/N₂ GAS MIXTURE AND PLASMA PARAMETERS

A. S. Chiper^{*}, N. Apetroaei, G. Popa

Plasma Physics Department, Faculty of Physics, "Al. I. Cuza" University,
Blvd. Carol I, No. 11, 700506 Iasi, Romania,

Present study refers to the influence of the percentage of nitrogen mass flow rate within a constant helium flow on the polymer surface treated by DBD plasma produced in He/N₂ gas mixture. The DBD plasma has been characterised by rotational temperature measured from molecular spectra of N₂⁺ molecules and intensities of spectral lines of He, N₂, N₂⁺ and OH respectively while the electrical parameters of the DBD were measured as amplitude of both discharge voltage and discharge current. Modification of the surface properties produced by the DBD plasma on polymer (PET+TiO₂) sample has been determined by AFM technique and measurements of the contact angle.

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1. Introduction

A large interest is still growing for Dielectric Barrier Discharges (DBD) due to their large area of applications as: surface treatment, pollutant destruction, ozone generation, excimer UV lamps, CO₂ lasers, plasma display panels and others. The DBD plasma is non-equilibrium highly collisional plasma produced at rather high gas pressure by a high voltage pulse applied to a special system of electrodes [1-3]. Depending on the composition of the gaseous mixture and operating conditions (applied voltage, excitation frequency and gas nature), different discharge modes of DBD were observed: filamentary discharge (FD) and homogeneous discharge (also referred to as Atmospheric Pressure Glow Discharge, APGD). Moreover, the APGD is realised in two forms: Townsend discharge (as, e.g., APGD in N₂) and glow discharge (such as, APGD in noble gases). It was demonstrated that the DBD in Townsend regime is characterised by the absence of the positive column and the maximum of the light intensity is localised near the anode, while a glow discharge regime present three distinguish areas (a positive column, a Faraday dark space and a cathode and a negative glow, which are not separated at atmospheric pressure) [4-7]. Accordingly, in the present paper we discuss about an APGD in He, or better glow discharge in He.

Massines et. al have demonstrated the influence of the discharge regime and the gas nature on the polypropylene surface treatment. Namely, in N₂ no significant effect of the discharge regime has been observed, because electrons and metastables lead to the same active species throughout the gas bulk, while the discharge regime have a large influence on the wettability of polypropylene treated in DBD in He. Thus, it was demonstrated that GD regime is more efficient on the polypropylene surface treatment than FD regime. [6-9]. In this paper was studied the influence of the percentage of the nitrogen mass flow on the polymer surface treated by DBD in He/N₂ mixture.

Briefly speaking, the aim of this paper is to contribute to a better understanding of the mechanisms, which conducted to the polymer surface modifications using the DBD plasma, and to

^{*} Corresponding author: alina.chiper@uaic.ro

correlate these experimental results with the results, which we obtained from diagnosis of the plasma.

2. Experimental set-up and experimental conditions

The experimental set-up (Fig. 1) consists of two copper plane-parallel electrodes of 10.4 cm^2 ($1.6 \text{ cm} \times 6.5 \text{ cm}$) surface area each. Two glass plates of 1.2 mm thick and 30 cm^2 ($3.4 \text{ cm} \times 8.8 \text{ cm}$) surface area each were used as dielectric barrier between the two copper electrodes. The distance between the two glass plates was 2.5 mm . Moreover, the copper electrodes were plated by magnetron sputtering on external side of each glass plate. One electrode was connected on high voltage and the other one was grounded. The high voltage power supply (1 to 20 kV) generates mono or bipolar sine pulses, width of 10 to $45 \mu\text{s}$ and frequency in the range of 10 Hz to 10 kHz. Total pressure of the gas mixture was in range 1.01 to 1.1 bar. The polymer sample was placed on a support between the two glass plates using a frame support of $4.2 \text{ cm} \times 3 \text{ cm}$, which was made of a rigid polymer. This support was manipulated with help of a shaft attached to the frame. Sample was made of polyethylene terephthalat containing titanium dioxide (PET+TiO₂). The polymer sample was placed between two electrodes at approximately same distance of both electrodes, so the polymer sample was floating within discharge plasma.

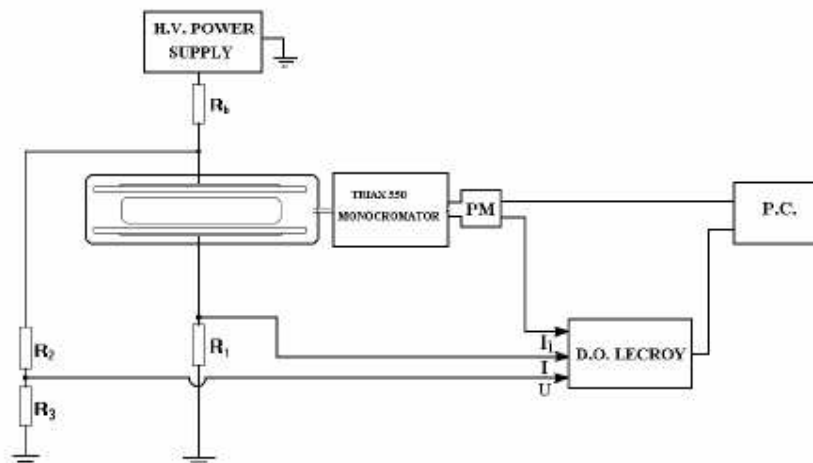


Fig. 1. Experimental set-up, $R_b=7,5 \text{ k}\Omega$, $R_1=150 \Omega$, $R_3/R_2=1000$.

The light emission of DBD plasma was analysed using Triax 550 spectrometer, which has a photomultiplier as detector. Potential (U) applied on the electrodes and current intensity (I) through the system have been measured using a digital oscilloscope (LeCroy 9304CM). The current intensity was measured via voltage drop across the resistance $R_1=150 \text{ W}$ connected series to the ground as in Fig. 1. The voltage across the copper electrodes was also measured using the resistance system R_2 , R_3 (Fig. 1). The time constant of the equivalent RC circuit was less than 0.5 ns . More details about the current and voltage shape of the DBD discharge are presented in [10].

In general, the role of the dielectric into DBD gap is to limit the amplitude of the discharge current [1,2,14]. Moreover, the influence of the dielectrics thickness, in the range of $\sim 1 \text{ mm}$ to 4 mm , on the magnitude of the amplitude of the discharge current through the DBD was already demonstrated [14]. In present experiments, the presence of the sample as additional dielectric between the electrodes must not have important effect on electrical properties of the DBD because the thickness of the dielectric sample is much smaller ($\sim 0.02 \text{ mm}$ - 0.1 mm) than the thickness of the dielectric glass plates (2.4 mm), which are comparable with those reported in [14]. Furthermore, the permittivity of the PET+TiO₂ is about 3, while the permittivity of the dielectric (alumina) used in [14] was 9. More precisely, in case of spectral and electrical diagnosis, the thickness of polymer sample was $100 \mu\text{m}$, while in case of surface treatment the thickness was $20 \mu\text{m}$.

Moreover, during the spectral and electrical measurements, the polymer sample was large enough to cover entire electrode area, while in the case of surface treatment the polymer sample was floating between the two electrodes and its area was smaller than the electrode area.

The glow mode of the DBD plasma was used for surface treatment of PET-TiO₂ sample for both He and He/N₂ mixture. The amplitude of the discharge monopolar voltage was in the range of $U_d=1.75\text{--}2.5\text{ kV}$ and constant frequency ($f=2\text{ kHz}$) and width ($t=20\text{ ms}$) of the pulses. The treatment time was 60 s. Only one control parameter, the ratio Q_{N_2}/Q_{He} , was used during treatment of the polymer sample. The ratio Q_{N_2}/Q_{He} was changed by changing the nitrogen mass flow rate Q_{N_2} , but having always a constant mass flow rate of helium, $Q_{He} = 90\text{ sccm}$.

3. Experimental results

Electrical diagnosis and emission spectroscopy were used to analyse the DBD system during treatment of the polymer samples. Surface properties of the polymer film were analysed via measurements of the contact angle and by Atomic Force Microscopy (AFM) technique, respectively.

3.1. Electrical parameters of the DBD

Electrical parameters as amplitude of both discharge voltage and discharge current were registered under conditions when percentage of the nitrogen mass flow rate in the total mass flow rate of helium - nitrogen gas mixture was varied with or without polymer sample in the discharge plasma. Typical time evolution of the discharge current intensity is presented in the Fig. 2 for the DBD with and without polymer sample between electrodes, but the same gas pressure and composition and the same discharge potential. This result shows that polymer sample within DBD plasma has negligible effect on electrical properties of the system.

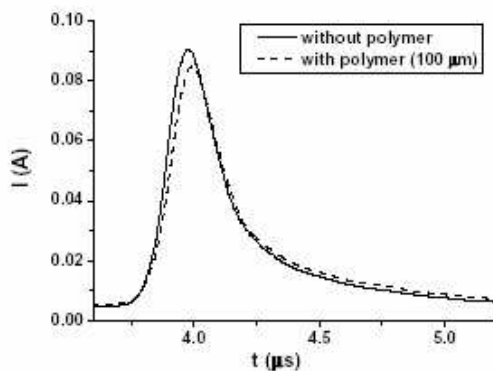


Fig. 2. Comparison between discharge current in the case of DBD with glass as dielectrics and glass-polymer as dielectrics.

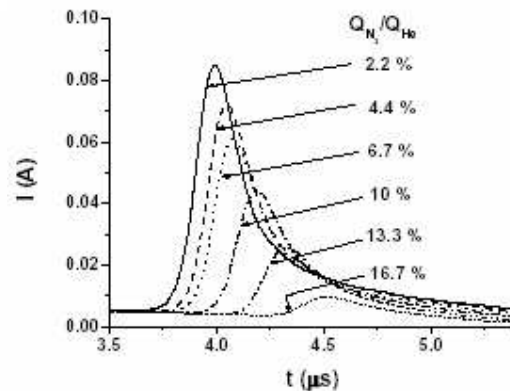


Fig. 3. Time evolution of the discharge current for different values of nitrogen mass flow in reactor, for $U_d=1.75\text{ kV}=\text{const.}$ and $Q_{He}=90\text{ sccm}=\text{const.}$

By increasing of the percentage of the nitrogen within the helium - nitrogen gas mixture an important change of the discharge impedance can be noticed. This fact is presented in the Fig. 3 where time evolution of the discharge current is presented for constant amplitude ($U_d=1.75\text{ kV}$) of the discharge voltage and constant mass flow rate of helium ($Q_{He}=90\text{ sccm}$), but having different mass flow rate of the nitrogen gas as parameter. It is obvious that both amplitude of the current intensity and total electrical charge for a single discharge decrease monotonically with increasing of the mass flow rate or better percentage of the mass flow rate of the nitrogen in the gas mixture. This result shows that increasing of the percentage of the nitrogen gas in the mixture time determines an increasing of the discharge impedance and consequently decreasing of the power transferred to discharge plasma.

3.2. Emission spectra of the DBD plasma

The species identified in our emission spectra are: He, N₂, N₂⁺ and OH. Presence of the OH radicals can be explained by following processes. One process is that of sputtering and decomposition of both polymer and TiO₂, respectively. Second process can be related to desorption and decomposition of the absorbed water by both polymer sample and the walls of the discharge chamber.

Variation of the emission intensities of He atom lines ($\lambda=587.6$ nm and $\lambda=706.5$ nm), N₂⁺ ($\lambda=391.4$ nm), N₂ ($\lambda=337.1$ nm) and OH ($\lambda=308$ nm) bands were investigated. Intensities of the atom lines and molecular bands exhibit different behaviour with respect to either constant amplitude of the discharge voltage or constant amplitude of the discharge current intensity in presence of the nitrogen in the mixture gas (Figs. 4-7). Thus, intensity of the He* spectral lines ($\lambda=587.6$ nm and $\lambda=706.5$ nm) decreases rapidly with the increase of the percentage (more than 3%) of the nitrogen mass flow rate in the gas mixture flowing through the reactor when amplitude of the discharge voltage was kept constant. On the contrary, in case of the constant amplitude of the discharge current, intensities of helium lines decrease very slowly with increasing of the same percentage of the nitrogen mass flow as for former case (Fig. 4).

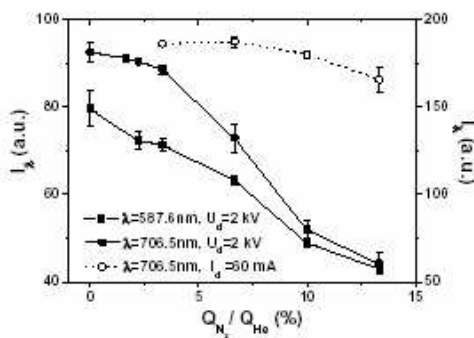


Fig. 4. Emission intensity of some He* lines versus percentage of the N₂ mass flow rate in He

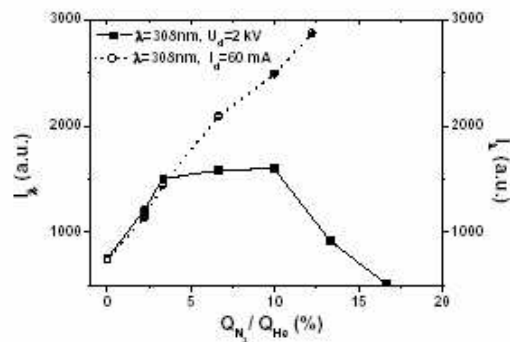


Fig. 5. Emission intensity of OH band versus percentage of the N₂ mass flow rate in He

Moreover, the intensities of the OH ($\lambda=308$ nm) and the N₂⁺ ($\lambda=391.4$ nm) and the N₂ ($\lambda=337.1$ nm) heads of the molecular bands present particular and pronounced behaviour with increasing of the percentage (more than 3%) of the nitrogen mass flow rate in the gas mixture flowing through the reactor and different conditions as constant amplitude of the discharge voltage and constant amplitude of the discharge current, respectively (Figs. 5-6). For constant amplitude of the discharge voltage ($U_d = 2$ kV), intensities of molecular bands versus percentage of the nitrogen mass flow rate have three distinct phases: (i) for low percentage of the nitrogen mass flow rate (up to 3%) considerable increase of spectral intensities can be measured; (ii) for percentage of the molecular nitrogen mass flow rate within total mass flow rate of the gas mixture more as about 4% but less as about 10 % variation of the spectral intensity is rather weak and (iii) a drastically decrease of spectral intensity of atomic lines and molecular bands for percentage of the nitrogen mass flow rate above about 10 %. Thus, intensity of OH band increases about 50% with increase to about 3% of the percentage of the nitrogen mass flow rate and then saturates and starts to decrease also rapidly for percentage above 10 % of the nitrogen mass flow rate in the helium mass flow rate (Fig. 5). Similar behaviour is measured also for heads of the molecular bands of the both N₂ and N₂⁺ molecules (Fig. 6). On contrary, for constant amplitude of the discharge current ($I_d = 60$ mA), intensities of the head of the OH, N₂ and N₂⁺ molecular bands increase with the increase of the nitrogen mass flow rate in the entire range of the total mass flow rate of the gas mixture through the reactor (Figs. 5 - 6).

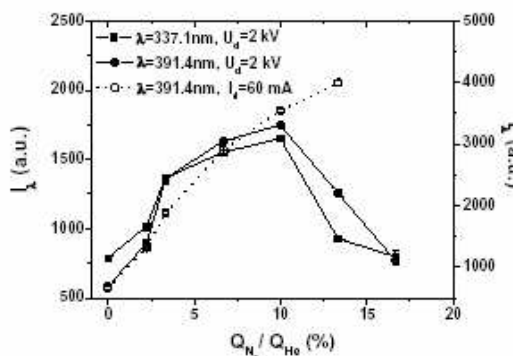


Fig. 6 Emission intensity of N₂ (l=337.1 nm) and N₂⁺ (l=391.4 nm) band heads versus percentage of the N₂ mass flow rate in He.

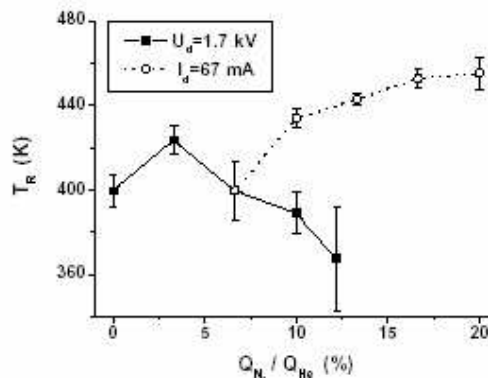


Fig. 7 Rotational temperature, calculated for N₂⁺ (l=391.4 nm) versus percentage of the N₂ mass flow rate in He.

Rotational temperature of the N₂⁺ population versus percentage of the nitrogen mass flow rate is presented in Fig. 7. It also shows that rotational temperature increases about 8 % with increase of the control parameter Q_{N_2}/Q_{He} up to about 3 % and then starts to decrease. But, for constant discharge current intensity, rotational temperature presents similar behavior to those presented in Figs. 5 and 6. More precisely, rotational temperature increases with increasing of the percentage of the nitrogen mass flow rate in the total mass flow rate of the gas mixture even beyond the limit of the control parameter $Q_{N_2}/Q_{He}=12.2$ (%) for which the GD mode ceased for constant discharge voltage.

3.3 Measurements of the contact angle and calculation of the surface energy

Information about energetic properties of the surface as: adhesion work, polar and disperse components of the surface tension [15] were obtained by the method of the contact angle for both untreated and treated polymer samples.

As was already mentioned during the surface treatment of the polymer sample all parameters listed above (total pressure and mass flow rate of helium, amplitude of the discharge current or of the discharge potential) were maintained constant and only one control parameter was used. This parameter was the percentage of the nitrogen mass flow rate in the constant mass flow rate of helium.

Firstly, for surface treatment of the polymer samples the amplitude of the discharge voltage was maintained constant, $U_d=1.75$ kV, and then the same experiment was made for another constant value of the amplitude of the discharge voltage, $U_d=2$ kV (Fig. 8). Immediately after DBD treatment in pure He, the contact angle for distilled water and for formamide (37%) have been measured. Decrease of the contact angle for distilled water from 83,3° for untreated PET+TiO₂ to 49,7° for treated PET+TiO₂ in He discharge was measured. This decrease corresponds to an increase of the adhesion work of the polymer surface (Fig. 9). If a low percentage of the mass flow rate of N₂ is added to pure He in the range of about 3 to 6 %, the contact angle decreases more than when the PET+TiO₂ sample was treated in pure He. By increasing the percentage of the mass flow of N₂ over about 6 % in He, an increase of the contact angle and a saturation of its value is observed. This saturation value of the contact angle is rather close to that one of untreated PET+TiO₂ sample (Fig. 8). Consequently, the same effect is observed for adhesion work (Fig. 9) and of course for both disperse and polar components [15].

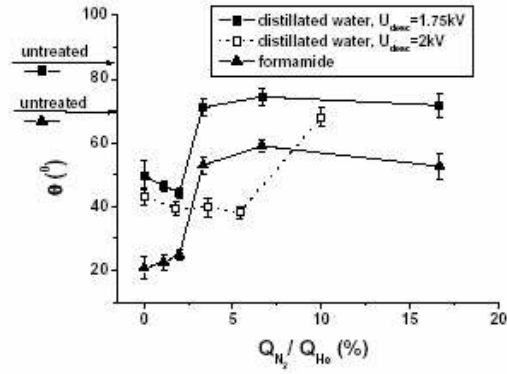


Fig. 8. Contact angle versus percentage of the N_2 mass flow rate in He/ N_2 gas mixture.

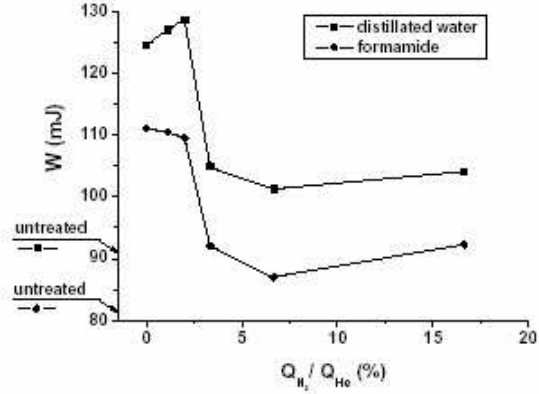


Fig. 9. Adhesion work versus percentage of the N_2 mass flow rate in He/ N_2 gas mixture.

3.4. AFM analysis

The Atomic Force Microscopy working in tapping mode was used for investigation of the polymeric surface morphology. AFM measurements are repeated on the same site of the sample under the same ambient atmosphere and room temperature. A particular attention has been paid for scanning the same area of $3 \mu m \times 3 \mu m$ of the polymeric sample before and after treatments. This fact was possible because the AFM images of PET+TiO₂ samples, for both untreated and treated in DBD plasma, are characterized by presence of rather pronounced peaks, which appear better emphasised after plasma treatment (Fig 10). The AFM $z(x,y)$ maps are used to estimate some texture parameters allowing for surface roughness characterization, respectively R and $rms R$, defined as:

$$\bar{R} = \frac{1}{x_{max}} \int_0^{x_{max}} |z(x)| dx \quad \text{and} \quad R_{rms} = \sqrt{\frac{1}{x_{max}} \int_0^{x_{max}} z^2(x) dx} \quad (1)$$

where $z(x,y)$ is the height of the surface element at point (x,y) and x_{max} the maximum value of the lateral displacement x during the measurements, for a given value of y .

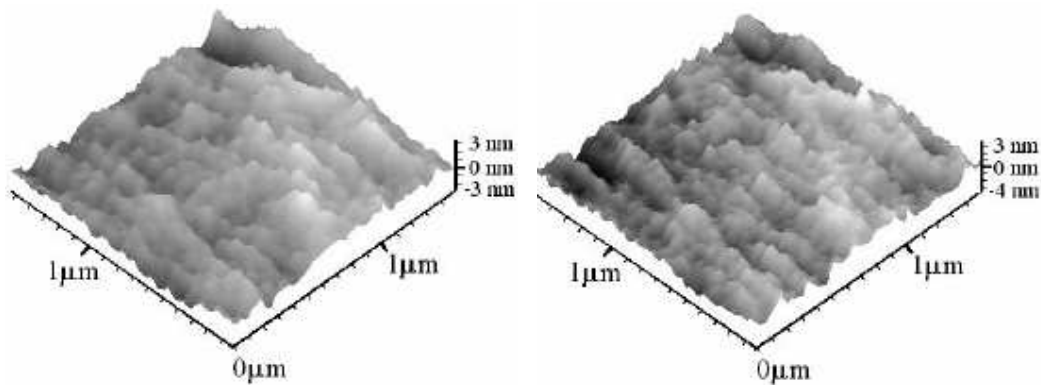


Fig. 10. 3D AFM images for untreated (a) PET+TiO₂ sample ($R_{rms} = 1.055$ nm, $R_{abs} = 0.858$ nm) and treated ($R_{rms} = 1.107$ nm, $R_{abs} = 0.905$ nm) one (b) using helium – nitrogen DBD plasma, for $I_d = 80$ mA=const. and $Q_{N_2} / Q_{He} = 7.8$ %.

Surface roughness was calculated for samples treated in helium and helium – nitrogen plasma, respectively, for the same value of discharge current ($I_d=80 \text{ mA}$). It shows that the difference between the treated surface roughness and the untreated ones is less as 5 % (Fig. 10).

4. Discussions

The experimental results presented in section 3 show that presence of the polymer sample in the DBD has practically negligible effect at least on electrical parameters, while, adding of the nitrogen gas besides helium as buffer, dielectric barrier discharge may change both electrical and plasma parameters of the discharge and consequently influence the process of surface treatment of the polymer sample by DBD plasma.

The former conclusion is proved by results presented in Fig. 2 where the electrical charge q crossing the discharge region was calculated as:

$$q = \int_{t_1}^{t_2} I(t) dt \quad (2)$$

for both cases without and with polymer sample within DBD plasma. Calculation was made taking as limits of the integral $t_1 = 3.4 \text{ ms}$ and $t_2 = 5.4 \text{ ms}$, respectively, in both cases. The difference between the two electrical charges, $q_{\text{without polymer}}=27.4 \text{ nC}$ and $q_{\text{with polymer}}=28.1 \text{ nC}$, is less as 2.3%.. Consequently, it might be considered that presence of the polymer sample within discharge plasma does not significantly change electrical properties of the system. This conclusion is also sustained by the fact that the capacitance of the system calculated in each of the two cases shows any considerable difference. It might conclude that the presence of the thin polymer sample into DBD gap has no significantly change of the electrical properties of DBD circuit.

The latter observation is demonstrated by results presented in Fig. 3 where the experimental results shows clear decreasing of the discharge current intensity and consequently of the total electrical charge with increasing of the percentage of nitrogen in helium – nitrogen gas mixture. Using relation (2) this time with the limits: $t_1=3.5 \text{ ms}$ and $t_2=5.4 \text{ ms}$, respectively, the result from Fig. 11 has been obtained. The total electrical charge q , crossing discharge plasma during the discharge pulse, decreases 20 times for an increase of the control parameter, Q_{N_2}/Q_{He} , of 7.5 times. This phenomenon has been already observed and explained as a consequence of the decrease of the ionization efficiency through Penning process [10, 16,17]:



where, $\text{He}^*(2^3\text{S})$ represents the metastable state of helium atom, e denotes the electron and N_2 and N_2^+ the nitrogen molecule and nitrogen molecular ion, respectively.

Besides, more nitrogen molecules in the discharge system more energy stored within internal degree of freedom of the N_2 molecule. The large number of electronic, vibrational and rotational energetic states of the N_2 molecule facilitates conditions for kinetic energy transfer, by electron–molecule collisions, from electrons to internal energy of the excited states of N_2 molecule. As a result the electron cooling process takes place and consequently, number of energetic electrons able to ionise helium atoms and nitrogen molecules decreases and both plasma density and electrical conductivity of the discharge plasma decrease.

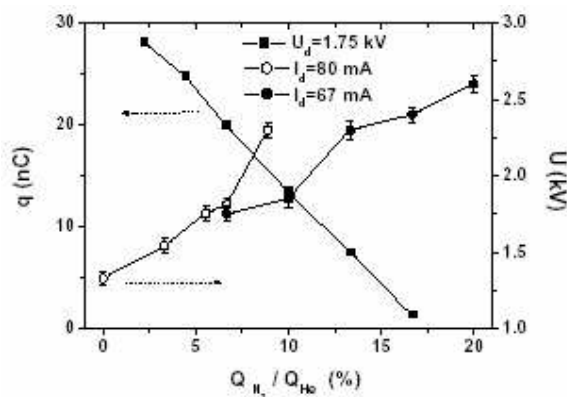


Fig. 11. Total electrical charge q during the discharge pulse and amplitude of the discharge voltage versus percentage of the N_2 mass flow rate in He/N_2 mixture.

In order to maintain same plasma density and consequently same density of active plasma species, the number of energetic electrons has to be increased with increasing of nitrogen percentage in the discharge gas mixture. Kinetic energy of the electrons can be increased by increase of the electric field intensity, which means increasing of the discharge voltage.

Moreover, the amplitude of the discharge current, and eventually total electrical charge, q , carried by a pulse, can be considered as first approximation of the discharge parameters by which may estimate plasma density. Consequently, experiments were made at constant amplitude of the discharge current and almost constant total electrical charge during the discharge pulse, but only for a restricted range of nitrogen percentage in the mixture (e.g., 0-6 %). In Fig. 11 it is presented dependence of the discharge voltage necessary to maintain the same amplitude of the discharge current intensity on percentage of the nitrogen in the helium – nitrogen gas mixture as control parameter. With increasing of the control parameter Q_{N_2}/Q_{He} of about 3 times, the discharge potential must increase of about 1.5 times, in order to maintain same amplitude of the discharge current of $I_d = 80$ mA.

Increase of the discharge voltage at constant amplitude of the discharge current intensity means an increase of the power into discharge plasma, which can be a measure of the internal energy stored mainly by nitrogen molecules. This increasing of the energy stored as internal energy of the atoms and molecules can explain results presented in Figs. 5 – 7 with respect to increasing of the molecular band intensity of the OH, N_2 and N_2^+ molecules with increasing of the nitrogen percentage in the gas mixture but constant amplitude of the discharge current.

Taking into account the results obtained and presented above on plasma properties and electrical characteristics of the dielectric barrier discharge with respect to the percentage of the mass flow rate of N_2 in the helium – nitrogen gas mixture the results obtained on surface treatment of the polymer sample can be discussed.

It is well known that treatment of the polymer samples in He plasma is rather efficient for producing cross-linking process at the polymer surface, due to helium metastable species. Plasma treatment in reactive gases (as N_2 , O_2 , etc.) produces functionalization of the polymer surface. Moreover, it must be mentioned that functional groups are formed at the surface of the polymer sample only under plasma treatment. Therefore, treatments in He/N_2 plasma are recommended for surface functionalization simultaneously with a cross-linking reaction. [11-13]

The surface functionalization of PET+TiO₂ sample is proved either by the decrease of the measured contact angle of distilled water (Fig. 8) or by the increase of adhesion work on treated samples compared with the untreated ones (Fig. 9). This process can be observed when the sample is treated either in He or in a mixture of He/N_2 with a low mass flow percentage of N_2 (up to about 3 to 6 %, depending on the electrical energy deposited into discharge). For higher percentage of the nitrogen mass flow rate (>10%) the measured values contact angle for distilled water was about same as that of untreated sample. The same effects are observed for the DBD in He/O_2 mixture. This effect might be a result of three different processes: (i) depopulation of the metastable levels of He

due to Penning effect, (ii) increase of the rate of surface oxidation [12,13] in the case of He/O₂ mixture and (iii) increase of the rate of surface oxidation because of oxygen atoms which result from the adsorbing water at sample surface. But, according to the results presented in Figs. 3 and 11 it is obvious that at constant discharge voltage, the amplitude of the discharge current decreases rapidly with increasing of the percentage of the nitrogen so that fluxes of the active particles arriving and reacting with the surface of the polymer sample decrease too. That may explain the fact that for higher percentage of the nitrogen in the gas mixture the modification of the polymer surface becomes very weak or even absent.

The results obtained by AFM are restricted mainly to 3D images of the untreated and treated polymer samples. Investigations made in a rather broad range of parameters as discharge voltage, amplitude of the discharge current intensity and percentage of nitrogen within helium – nitrogen gas mixture show that plasma treatment does not significantly change the morphology of the surface. But modification of the contact angle and accordingly of the surface energy shows that plasma treatment is mainly at atomic and molecular level.

5. Conclusions

The experimental results allow the following main conclusions:

1) Adding molecular nitrogen as a reactive component to helium buffer gas in a dielectric barrier discharge produces an increase of the discharge impedance caused by decreasing of plasma density and conductivity.

2) Increasing of surface energy of the PET+TiO₂ sample by action of the nitrogen – helium DBD plasma is possible for lower percentage of nitrogen (up 6%) in the mixture.

3) Modifications induced by plasma particles on the surface of the polymer sample under experimental conditions presented in this paper are at atomic and molecular level, so that the AFM technique does not reveal significant modification of the surface morphology.

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