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ADHESIVITY IMPROVING OF PET BY TREATMENT IN LOW PRESSURE PLASMAS GENERATED AT 40 kHz AND 1 MHz. COMPARATIVE STUDY

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Abstract. A comparative study on the surface activation of polyethylene terephtalate by treatment with subatmospheric pressure air plasmas, generated at 40 kHz and 1 MHz, was made. The activation effect was evaluated by measurements of contact angle and of force required to detach the bonded polyethylene strips and by AFM examination.

Keywords: low pressure plasma, surface treatment, contact angle, bonding force, atomic force microscopy.

1. INTRODUCTION

Over the last decades the interest for polymeric materials has continuously increased due to their multiple applications in medicine, food industry, electronics, automotive industry and many others [1–5]. Polymers have excellent characteristics (lightweight, mechanical and chemical resistant, easy to process and model, recyclable) but in the same time their surface energy is relatively low [6]. The latter property represents an important deficiency when polymeric materials need to be painted or bonded together [7]. One of the most used methods for increasing the surface energy of solid materials is the plasma treatment. The interaction of the radiation and active species (molecules, ions, atoms) generated in plasma with the polymer surface can increase the surface energy by breaking chemical bonds and producing radicals able to react with other active species from paint or bonding materials. Moreover, the etching process which takes place when the solid surface interacts with the heavy particles (especially energetic ions) from plasma, determines an increase of the active area of the polymer surface.

During the last years the attention was focused on the treatments with atmospheric pressure plasma (APP) generated in various gases (Ar, He, N_2, air or mixtures). The plasma must be thermally nonaggressive with polymers and it needs to be able to treat a large area of material. It is well known the fact that the plasma temperature and dimensions depend, besides other working parameters, on the frequency of the electric field from which the plasma absorbs its energy [1, 8–10]. At low frequencies (tens of kHz) APP is cold and large in volume while at higher frequencies (MHz) its temperature is higher and its volume is lower for an equal power transferred to the plasma in the two situations. This is the reason for which the most treatments of polymers with APP are performed using plasmas generated with electric fields having frequencies in the range of kHz – tens of kHz [11–17].

Only few studies evaluating the effect of the operating frequency [17] or of the gas pressure [18] on the surface characteristics of polymers treated with plasma were performed at subatmospheric pressure. Their most important conclusions were: (a) for a pressure of 40 mtorr the treatment effect on the surface energy and morphology of the air plasma generated at 40 kHz is more efficient than at a frequency of 13.56 MHz [17], and (b) in the pressure range of 10–90 mtorr and for plasma powers higher than 50 W no significant differences were observed between surfaces treated with plasma generated in argon [18]. Our aim was to compare the effect had by treatment in plasmas generated at very different frequencies of the electric field on the surface characteristics (wettability and morphology). In order to have the possibility to generate a cold plasma with a large volume using a frequency of the electric field of 1 MHz, we decided to work at subatmospheric pressure. The second frequency was 40 kHz. The other operating parameters (plasma gas, plasma power, gas pressure and plasma chamber volume) were identical. Polyethylene therephtalete (PET), as one of the most used synthetic material in various applications, particularly in medical ones, was chosen for our study.

2. MATERIAL AND METHODS

In order to generate the subatmospheric pressure plasmas, two dielectric barrier discharge generators, working on the same principle, were used. The first of them, working at 40 kHz, is a commercial one: Zepto, Diener Electronic. Because a similar commercial generator working at 1 MHz was not available, a laboratory-made generator with the same plasma chamber geometry as Zepto was designed and built. Details on the running principle and the full description of the electric circuit can be found in [19].

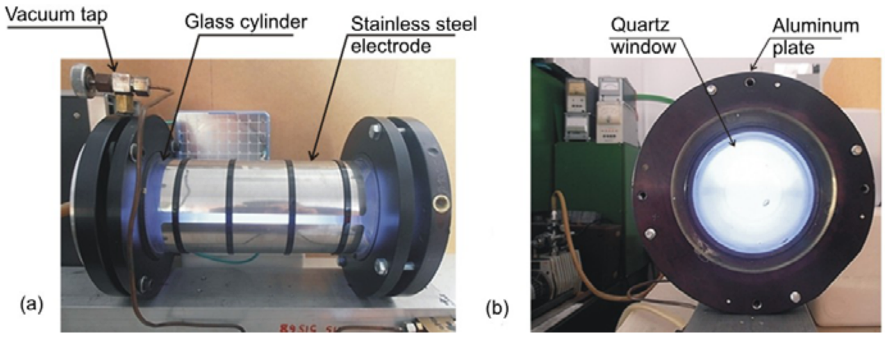

Fig. 1 – Laboratory-made plasma chamber for 1 MHz generator: (a) lateral view, and (b) end view.

The plasma chamber is a glass cylinder with an inner diameter of 100 mm and a length of 300 mm (Fig. 1). The glass wall (7 mm thickness) also represents the dielectric barrier of the discharge. Two metallic electrodes made from stainless steel sheet (0.8 mm thickness) are placed outside the chamber. One of them is connected to the output of high frequency generator and the other one is grounded. The two ends of the glass cylinder are closed with aluminium disks equipped with rubber O-rings for sealing. The radiation of the plasma was monitored through a quartz window mounted on one of the aluminium disks. During the PET treatment the operating parameters of the two generators were identical: 0.4 mbar (300 mtorr) air pressure and 80 W plasma power.

Plasma characterization was made by monitoring the plasma optical emission spectra using an Ocean Optics High-Resolution Fibre Optic Spectrometer HR4000CG-UV-NIR for wavelengths between 200–1100 nm *via* PC employing the dedicated software SpectraSuite (Ocean Optics Spectroscopy Platform). Atomic and molecular emitting species identification and labelling were performed using the Spectrum Analyzer software. The gas temperature was measured using a small alcohol thermometer and was also estimated with a sheet of Temperature Sensitive Liquid Crystal (TSLC) sheet (Edmund Optics). The both sensors were immersed inside plasma chambers without disturbing the discharge because they are made from dielectric materials.

For bonding strength tests, three sets of PET strips (70 mm length, 6 mm width) tailored from bottle grade PET were used. The strips from the first set were cleaned with isopropyl alcohol and then they were bonded in pairs. They were used as reference samples. Before their bonding in pairs the other two sets of strips were first cleaned and then treated separately in the two air plasmas generated at 40 kHz and at 1 MHz, respectively. The used adhesive was a commercial one (Poxipol) with a hardening time of 20 min. In all cases the bonding surface was 6×6 mm^2.

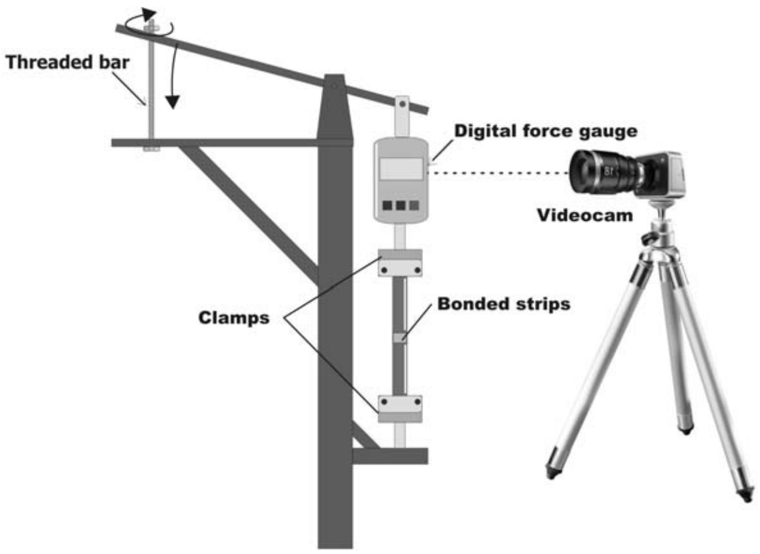

Fig. 2 – Schematics of the bonding strength testing device.

The bonding strength tests were performed with a laboratory made device consisting of a mechanical lever system actuated by a threaded bar. It is sketched in Fig. 2. The bonded strips are clamped at the two ends and are fixed between the fixed and the mobile arms of the lever via a commercial digital force gauge having resolution of 0.1 N. By acting the mobile arm of the lever, the strips are stretched in longitudinal direction with a test speed of about 15 mm/min until their failure (separation of one strip from adhesive). According to metrological standards, such a test is called "lap-shear strength test" and the results, called "the maximum shear strength", are expressed in kg/cm^2 or in pressure units (N/m^2). The value of the force displayed in the separation moment was read using a digital camera set to movie mode. The final result is the average of five measurements carried on five pairs of identically treated and then bonded strips. It was used for calculation of maximum shear stress.

The wettabilities of the PET surfaces were evaluated by contact angle measurements. They were made by placing 2 μl of deionized water droplets on the PET strips using a micropipette. The image of a droplet was taken using a commercial digital camera (Nikon Coolpix P500, 14 MP× resolution). The values of the contact angles were measured using the ImageJ free image processing software [20]. The final value of the contact angle is the average of five measurements.

The surface roughness of the untreated (taken as reference) and plasma treated strips was examined at ambient temperature by atomic force microscopy (AFM) with a NT-MDT NTEGRA Spectra microscope. Images were taken in dynamic intermittent contact mode with a silicon cantilever (NSG30-A, NT-MDT) whose nominal spring constant was 40 N/m and whose tip radius of curvature was less than 10 nm. After acquisition, image processing was performed using Nova v1.1.0.1837 (NT-MDT) SPM software for flattening.

3. RESULTS AND DISCUSSION

The optical emission spectra of plasmas generated under the same working conditions at 40 KHz and 1 MHz are shown in Fig. 3.

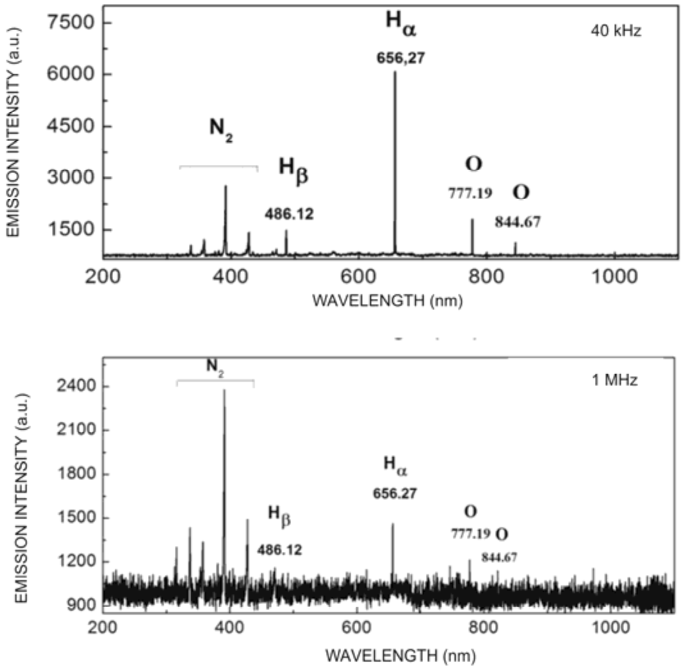

Fig. 3 – Emission spectra of plasmas generated at 40 kHz and 1 MHz.

The emissions of both plasmas contain atomic lines and molecular bands corresponding to the same species: hydrogen and oxygen atoms and nitrogen molecules. Hydrogen atoms are the result of dissociation in plasma of water molecules from air (moisture) and nitrogen and oxygen are the main components of air. In terms of emission intensity, the plasma generated at 40 kHz has more intense and better resolved emission lines compared to the plasma generated at 1 MHz. The chemically reactive species generated in plasma, especially oxygen and OH radical, induce the formation of polar functional groups and determines an important increase of the polar fraction of the surface energy of the treated material

[6]. For example, it was shown that the PET surface energy can be increased from 27.5 mJ/m^2 to 57 mJ/m^2 by a one minute treatment with 40 kHz low pressure (40 mbar) air plasma [17]. Moreover, a treatment in plasma for tens of seconds can induce significant changes in the surface morphology and roughness of PET.

The gas temperature (also known as kinetic temperature) measured with the thermometer was 35–36 °C for both plasmas. This value was confirmed comparing the colour of the TSLC sheet with the scale from the datasheet and it demonstrates the thermally non-aggressive character of both plasmas.

The effect of the plasma treatment on the adhesivity of PET strips was evaluated by shear strength tests. The dependence of the shear strength on the duration of the plasma treatment is presented in Fig. 4. The tested strips were bonded immediately after the treatment. On the one hand, it can be noticed that for both plasmas the maximum shear stress increases rapidly after only two seconds of plasma treatment and then it presents a saturation tendency. On the other hand, the maximum shear stress for the samples treated in the plasma generated at 1 MHz is higher than the one in the case of the treatment in the plasma generated at 40 kHz what means that the treatment at higher frequencies is more efficient for the improvement of PET adhesivity. It is important to mention that after only a very short treatment time (2 s) the bonding efficiency is of 3–4 times higher than without plasma treatment. The higher efficiency of the treatment in plasma generated at 1 MHz can be explained based on the mechanisms that contribute to the improvement of the materials adhesivity: the increase of the surface energy and the changes in the surface morphology and roughness which determine an increase of the effective surface area (the surface to be bonded) [17]. As it will be shown further, because the plasma generated at lower frequencies is more efficient in the increase of the surface energy, we suppose that the second mechanism (the changes in the surface morphology and roughness) could be more effective at higher frequencies.

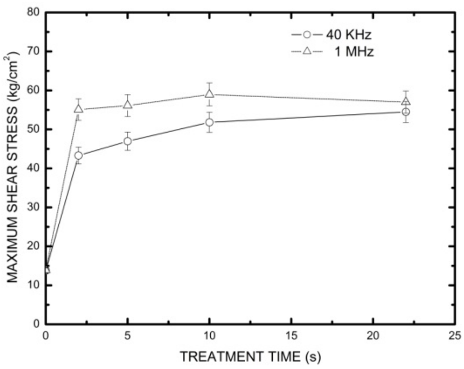

Fig. 4 – Dependence of shear strength on the treatment time in plasma.

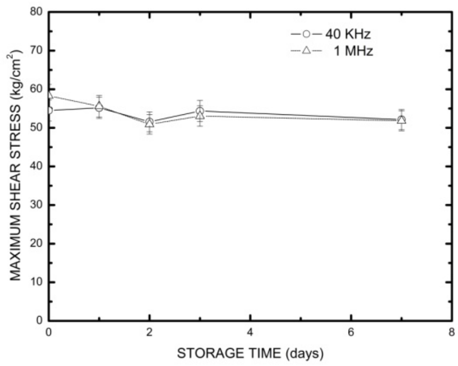

Fig. 5 – Evolution of shear strength after the treatment in plasma.

In order to find the durability of the plasma treatment, aging tests were performed. The maximum shear stress was measured for different pairs of bonded strips immediately after the plasma treatment and after 1, 2, 3 and 7 days. The strips were treated for 22 seconds in the plasma generated at 40 kHz or 1 MHz and were stored in a closed container until the bonding strength test. The results are presented in Fig. 5. As it can be observed, the time evolution of the adhesivity of the samples treated at the two frequencies is slightly different. While for the samples treated in the plasma generated at 40 kHz the aging process is slow and relatively uniform, for the samples treated at 1 MHz it is more pronounced in the first two days and then it becomes slow. After two days of storage the maximum shear stress is reduced with 5% in the case of activation at 40 kHz and with 13% in the case of activation at 1 MHz. It is worth mentioning that after two days of storage the maximum shear stress for samples treated in the two different plasmas are very close. These results suggest that further processing of the samples treated in plasma can be done several days after the treatment.

To establish the contribution of each of the two mechanisms to the improvement of the PET adhesivity (the increase of the surface energy and the changes in the surface morphology) contact angle measurements and AFM examinations were performed.

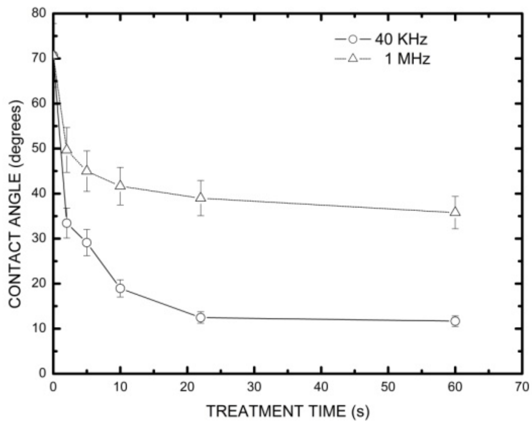

Fig. 6 – The dependence of contact angle on treatment time in plasma.

The changes in wettability (and implicitly in the surface energy) of the PET strips are directly related to the contact angle of deionized water droplets deposited on the material surface. Figure 6 presents the results of the contact angle measurements as a function of treatment time in plasma and Fig. 7 presents the results of aging tests.

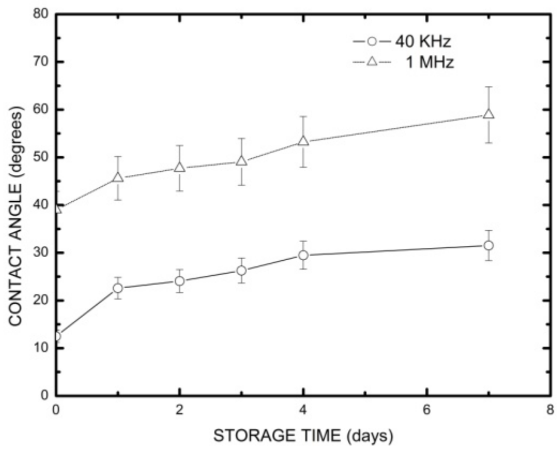

Fig. 7 – Evolution of contact angle throughout 7 days of study.

Figure 6 shows that in both cases the contact angle values have been significantly reduced with the treatment time, which means that the surface energy of the treated PET samples has increased after the plasma treatment. The increase of the surface energy is mainly attributed to the formation of polar functional groups on PET surface during the treatment process [21]. It can also be observed that the plasma generated at 40 kHz is more efficient in the increasing of the surface energy (reflected in the decreasing of contact angle) than the plasma generated at 1 MHz. During the same activation time (22 s, *e.g.*), the contact angle decreases with 58 degrees when the samples are treated at 40 kHz and with only 32 degrees when they are treated at 1 MHz. The decrease of the contact angle can be correlated with the adhesion work (the energy required to separate a unit area of two phases in contact, here water and PET respectively). Based on Yung's equation, the next formula can be used to calculate the adhesion work, W_A [21]:

$$W_A = \gamma_L(1 + \cos\theta), \qquad (1)$$

where γ_L is the surface tension or energy of the liquid (for water it is 72.8 mJ/m^2) and θ is the contact angle of the liquid placed on the solid surface. In our experiment, after 22 s of treatment, the adhesion work increased from 96.9 mJ/m^2 to 143.8 mJ/m^2 for samples treated in plasma generated at 40 kHz and to 129.4 mJ/m^2 for plasma generated at 40 kHz. We suppose that this difference is due to a higher density of active species occurring in the plasma generated at 40 kHz than in the plasma generated at 1 MHz, as it is revealed in the emission spectra of the two plasmas (Fig. 3). Figure 7 shows a linear increase in time of the contact angle after the samples treatment, with the same rate for the samples treated with the two different plasmas. Correlated with the time evolution of the shear strength

(Fig. 5), this suggests a slightly decrease of the surface energy while the surface morphology remains unchanged.

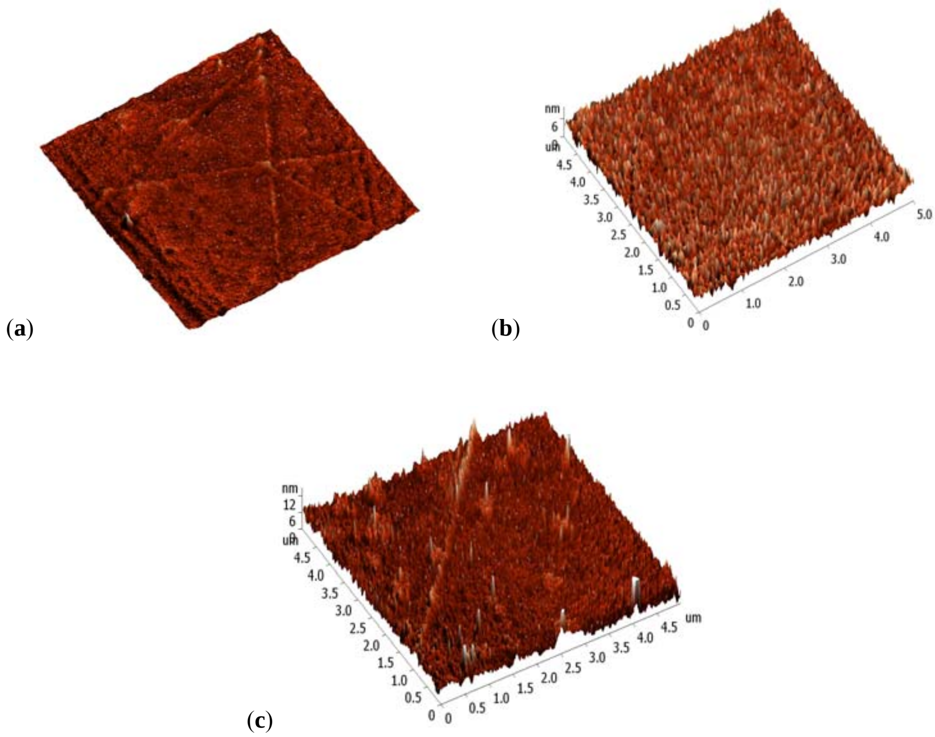

Fig. 8 – AFM images of the untreated sample (a) and of treated samples with 40 kHz (b) and 1 MHz (c) plasma.

The contact angle measurements, corroborated with the conclusions drawn after the bonding tests, support our assumption according to which when the PET samples are treated in plasma generated at 1 MHz, the less efficient activation by formation of polar functional groups than at 40 kHz is compensated by the more efficient activation by changes in the surface morphology and roughness of PET. For verifying this hypothesis, surface morphologies of the untreated and plasma treated (80 W, 22 s) samples were examined by AFM.

Figure 8a shows the topographic image of the untreated sample and figures 8b and 8c show the topographic images of the samples treated with 40 kHz and 1 MHz plasmas respectively. Average of roughness (R_a), root mean square roughness (R_{rms}) and surface skewness (S_{sk}) of each sample are summarized in Table 1. The studies were carried out over scan areas of 5 × 5 μm.

Table 1

Average roughness, root mean square roughness and surface skewness of the untreated and plasma treated samples

	R_a [nm]	R_{rms} [nm]	S_{sk}
Untreated	0.73	0.97	0.67
Treated at 40 kHz	0.99	1.24	0.16
Treated at 1 MHz	1.1	1.42	1.01

The AFM images and the values of the average roughness and of the root mean square roughness confirm that the treatment at 1 MHz is more efficient than the one at 40 kHz in order to induce changes in the surface morphology of the PET samples.

4. CONCLUSIONS

PET surfaces were treated in two sub-atmospheric pressure air plasma generated at 40 kHz or 1 MHz with the aim to estimate the influence of the working frequency on their adhesivity. Plasma treatment for only several seconds is able to increase the surface energy and to change its morphology and roughness and, as a consequence, to enhance the adhesion properties of the treated samples. The bonding tests and water contact angle measurements showed that the surface activation in air plasma generated at 1 MHz is more effective than the one at 40 kHz at least during a day after plasma treatment. Afterwards, the adhesivity of the samples treated using the two plasmas are comparable. The PET strips preserve their enhanced properties for few days after the activation process, the ulterior processing of the samples being possible with good results. The general conclusion is that by activation for only few seconds in a subatmospheric pressure air plasma generated at frequencies placed in the range of 10^4–10^5 Hz is possible to obtain PET structures with bonding strengths 3–4 times higher compared with the direct bonding after chemical cleaning.

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