Surface modification of polymers at atmospheric pressure in expanding RF plasmas generated by planar dielectric barrier discharges

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We present a small dielectric barrier discharge radiofrequency plasma source, operating at 13.56 MHz, having a rectangular configuration. The source generates a knife-like cold expanding plasma jet, suitable for polymer surface modification. The planar jet was characterized by thermocouple measurements and Optical Emission Spectroscopy which show low thermal loading at substrate and the presence of active plasma species. Polyethylene terephthalate, polyvinyl chloride for medical usage, polyethylene, polytetrafluoroethylene foils were treated in open atmosphere with the source working in argon. The modification of the treated surfaces was investigated by contact angle measurements, Atomic Force Microscopy and adhesion measurements. A substantial improvement of wettability and adhesion was obtained.

1. Introduction

Plasma treatment is a widely used technique for surface modification of materials, while maintaining unchanged the bulk properties. As effects of such treatments wettability can be enhanced, as shown for polyethylene terephtalate (PET) [1]. Even for materials which are extremely hydrophobic one may obtain a hydrophilization effect by plasma treatment, as example for polytetrafluoroethylene (PTFE) [2]. As the previous reports have shown the modification proceeds via the change of surface chemistry (chemical groups bonded at surface) and topography (roughness at micro and nanostructured) and can be realized using either low pressure or atmospheric pressure plasmas [3, 4].

Low pressure plasmas are suitable for a large number of applications in industry especially for the low temperature, which is intrinsic to their non-equilibrium nature. However, the technology needed for them to work (vacuum systems, movement under vacuum, large size equipment) is expensive. On the other hand, atmospheric pressure plasmas do not require such needs to work, making these an alternative to the low pressure plasma treatment [5]. Nevertheless, most of the atmospheric pressure sources produce equilibrium hot plasmas that cannot be applied to materials sensitive to thermal damage like polymers.

In recent years non-equilibrium plasmas at atmospheric pressure have been developed as effective tools for activating surfaces, based on bare electrodes or dielectric barriers discharges. The cold character of these sources makes them the logical choice in thermal sensitive materials processing.

In this paper we present a plasma source based on radiofrequency dielectric barrier discharge, its characteristics and we prove its suitability for modification of temperature sensitive substrates. The plasma produced by this source is investigated by means of Optical Emission Spectroscopy (OES), and the gas temperature was determined by means of thermocouple measurements. Polymer films of polyethylene (PE), polyvinyl chloride (PVC) for medical usage, polyethylene terephtalate (PET) and polytetrafluoroethylene (PTFE) were subjected to treatment with the plasma expanded from the DBD source. The effects of surface modification due to the treatment were examined by contact angle measurements, atomic force microscopy and scotch tape adhesion tests.

2. Experimental

The plasma source design (Fig. 1) is based on two trapezoidal aluminium electrodes, one of them supported by a ceramic plate of 1 mm thickness, arranged in parallel configuration, which define together with lateral insulating ceramic spacers a trapezoidal discharge gap with a larger opening at the gas entry and a narrow one at the plasma exit. During the source operation the ceramic plate and the lower electrode are facing the plasma. The role of the ceramic material is to prevent the contraction of the discharge and the transition to arc, the discharge current being self-limited by charge building-up on the dielectric surface. The plasma source is of small size (see scale in Fig. 1) with a rectangular exit (nozzle of 4 mm x 1 mm dimensions). The plasma jet starts from the nozzle and has a triangular shape, with a length of 9 to 10 mm.

The power is supplied to the discharge by a radiofrequency generator at 13.56 MHz via a matching network. The RF is connected at the back end of the source to one of the electrodes (RF powered electrode) while the opposite one is grounded.

The gas (argon of quality 5.0) is supplied to the discharge through a gas inlet applied to the largest part of the gap through a hole performed in the lower electrode (ground electrode).

For avoiding the perturbation of surrounding laboratory equipments by electromagnetic interferences, the grounded electrode is extended as a shielding enclosure for the entire DBD assembly; the distance between the upper part of the shield and the RF electrode is large enough for preventing undesired discharges in air between the shield and the DBD upper electrode.
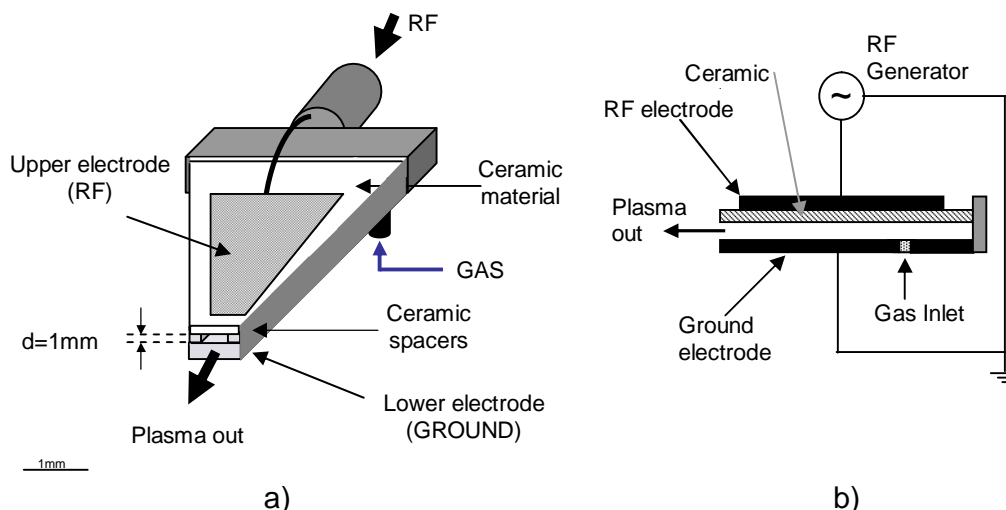

Fig. 1. The DBD source: (a) spatial view, (b) sectional view.

The device operates stable in argon at power levels of 6-50 Watts. The lower limit is established by plasma extinction, while the higher limit is set by excessive heating or discharge instabilities (filamentation). The used mass flow rates were in the range 500-10000 sccm. An image of the device and of the plasma expanding from the interelectrodic gap is presented in Fig. 2.
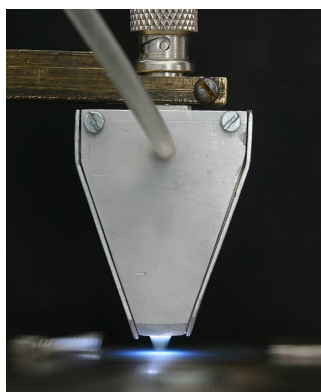

Fig. 2. Image of the DBD plasma jet at 20W and 5200 sccm in Argon flow.

The obtained plasma was characterized by OES. The spectra were recorded with a setup consisting of a 0.5 m Bruker spectrograph with Andor IDus CCD camera and 200 microns optical fiber. The entrance slit was set to 25 microns while the grating chosen for these measurements had 1200 traces/mm.

A special attention was paid to temperature investigation, this parameter being of high importance for processing of polymers. The gas temperature was determined by means of thermocouple measurements, and also by fitting the experimental OH radical spectra with simulated spectra.

The surface modification was performed by exposing the polymeric foils placed on an x-y translation stage to the expanding plasma jet generated by the DBD source. A selected area of 10 mm x 10 mm was treated with a variable number of scans. The scanning speed was 5mm/sec, the width of the plasma jet at 2 mm (distance to substrate) was 3 mm and the distance between paths was 1 mm.

The treatment experiments where done at a power of 15 W and 4500 sccm, for a plasma source to substrate distance of 2 mm. The plasma characterization measurements where realized at a power of 20 W and 5200 sccm.

Contact angle measurements were used to characterize the wettability of foils. The contact angle was measured by the sessile drop method, using distilled water as wetting liquid. The measurements were realized at room temperature by placing a drop of 0.5 µl of liquid on the surface. The error of the measurements is +/- 3 degrees.

The effect of atmospheric plasma treatments on the topography of surface was investigated by Atomic Force Microscopy (AFM). The measurements were done with a

Park Systems XE-100 which has a multi-mode operation: contact, non-contact, intermittent contact. This allows a maximum scanning area of 50×50 μm^2 and a vertical displacement of 12 μm.

The adhesion of the polymeric foils was investigated by the Scotch tape test from 3M-company. The 3M Brand Scotch tape test is a measuring technique suitable for evaluation the adhesion of coating films after plasma treatment. It consists in evaluating the force for detaching a Scotch tape away from the polymer foil. Details about this procedure can be found elsewhere [6].

3. Results and discussion

3.1 Plasma characterization

3.1.1 Optical emission spectroscopy

Fig. 3 presents an emission spectrum of the expanded DBD plasma recorded at 1mm distance from the nozzle using the setup described earlier. The emission was investigated in the spectral range 200-1000 nm, chosen to comprise the NO, OH, N_2, NH, molecular bands and Ar atomic lines.
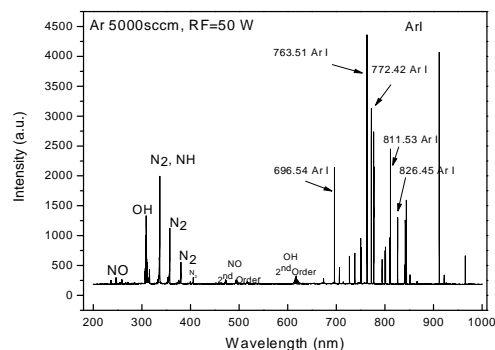

Fig. 3. Full spectrum of the DBD source at 50W RF power and 5000 sccm Argon flow.

The spectra show the presence of several Ar lines in the region 600 – 1000 nm, as well as the emission of molecular bands namely, the OH 3064 Å system ($A^2\Sigma^+ \rightarrow X^2\Pi$) and NH 3360 Å ($A^3\Pi \rightarrow X^3\Sigma$) system and the Second Positive System of Nitrogen (Table 1). The bands in the spectrum have been identified according to the reference [7].

Table 1. List of the most important lines and bands recorded at 1 mm from the expanding nozzle.

Species	Wavelength (nm) (lines or bands v''-v')		Spectral system (transitions)
NH	336.00	(0,0)	3360 Å System $A^3\Pi \rightarrow X^3\Sigma$
OH	308.9	(0,0)	3064 Å System $A^2\Sigma^+ \rightarrow X^2\Pi$
γNO	259.57 258.75 247.87 247.11 237.02 236.33	(0,3) (0,3) (0,2) (0,2) (0,1) (0,1)	Third Positive System $A^2\Sigma^+ \Leftrightarrow X^2\Pi$
N_2	337.04 315.87 357.52 380.45 405.84	(0,0) (1,0) (0,1) (0,2) (0,3)	Second Positive System (SPS) $C^3\Pi \rightarrow B^3\Pi$
Ar	912.29 811.53 772.37 763.51 696.54		$3s^2 3p^5(^2P^o_{3/2})4p - 3s^2 3p^5(^2P^o_{3/2})4s$ $3s^2 3p^5(^2P^o_{3/2})4p - 3s^2 3p^5(^2P^o_{3/2})4s$ $3s^2 3p^5(^2P^o_{3/2})4p - 3s^2 3p^5(^2P^o_{3/2})4s$ $3s^2 3p^5(^2P^o_{3/2})4p - 3s^2 3p^5(^2P^o_{3/2})4s$ $3s^2 3p^5(^2P^o_{3/2})4p - 3s^2 3p^5(^2P^o_{1/2})4p$

In spite of the fact that the feeding gas is argon, it is found that the spectrum is rich in molecular bands. The signatures of molecules like NO, OH, NH, N_2 could come from the gas impurities, but result also from the active mixing of plasma expanding from the interelectrodic space with the ambient air. The presence of such radicals is important for change of wetability because some of them are polar molecules.

3.1. 2 Temperatures in the expanding DBD plasma jet

It is known [8, 9] that at atmospheric pressure the gas temperature in plasmas can be assumed to be equal with the rotational temperature of the OH radical. In order to obtain the rotational temperature the bands of the OH 3064 Å system ($A^2\Sigma^+$-$X^2\Pi$) were recorded first. The OES experimental data were collected through the optical fibre placed at 1mm from the plasma jet axis. Afterwards, the OH experimental spectrum was fitted with a simulated one. The rotational temperature, which usually can be associated with the gas temperature, was extracted from

the fitting procedure. A recorded spectrum and the corresponding best fitted simulated spectrum are given as example in Fig. 4. Quite low temperatures, like 390 K, were calculated, which are peculiar to cold atmospheric pressure barrier discharges [10].
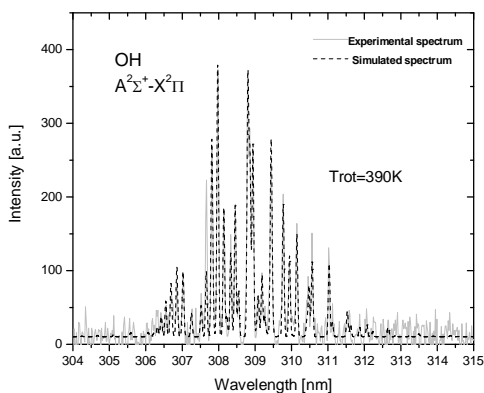

Fig. 4. Example of recorded and simulated spectra for the 308 nm OH molecular band (DBD plasma source jet, at 20W and 5200 sccm gas flow, 1 mm distance from the nozzle).

Temperatures were also measured by means of a thermocouple. For the same position as before (1 mm) a temperature value of 370 K was obtained, which indicate also a cold plasma character. The difference in the values of temperature obtained by the two methods is expected,

as the thermocouple measurements were not corrected for the cold junction absence and the rotational temperature calculations are affected by errors in a range of 10%.

3.2 Modification of polymer surfaces

3.2.1 Modification of the wettability

The measurement of the contact angle is the usual method for examining the properties of the surface with relevance to dyeing, bonding by adhesives or functionalization by grafting with molecules having hydrophilic groups.

The variation of the contact angle gives a quantitative measure of the wettability modification. Fig. 5 presents the changes of contact angle values for PE, PVC, PET and PTFE surfaces, with an increasing plasma treatment time. The decrease of contact angle is visible for all materials, being lower for PTFE. The modification dynamics indicates two treatment stages, an early stage characterized by a fast decrease of the contact angle, and a late stage characterized by a slow modification rate. It can be observed that the most prominent decrease of the contact angle occurs for PET and PE (56% for both materials, after only 1sec/mm^2).
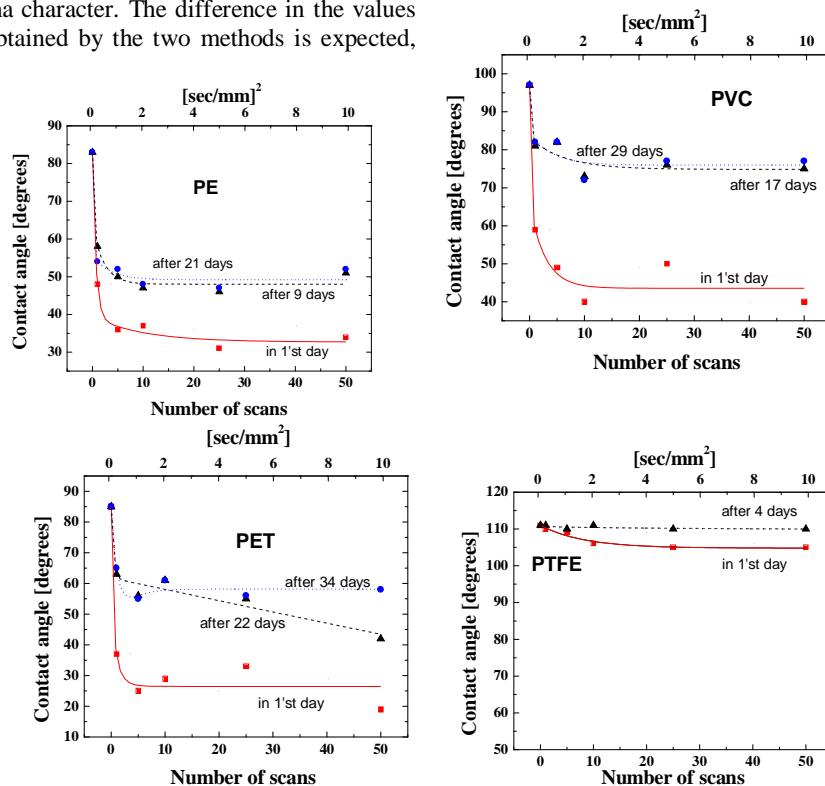

Fig. 5. Dependences of the contact angle with the number of scans for PE, PVC, PET and PTFE.

First factor responsible for decreasing the contact angle is the chemical activity of plasma, which create at surface active sites by breaking the local chemical bonds. The surface is then enriched in polar groups by insertion at these sites of radicals or chemical groups containing oxygen [11] taken from plasma or the ambient atmosphere. In addition, physical etching and sputtering of low-molecular weight molecules from surface leads to changing of surface morphology (roughening). Both effects (chemical and morphological) lead to wettability improvement, which is described by the decrease of the contact angle [12, 13, 14].

In respect with the only minor modification of PTFE, the small change in the contact angle might be due to the difficulty of changing the surface chemistry. The formation of active sites is more difficult on the surface dominated by CF bonds (breaking energy 490 kJ/mol) as compared to the surface dominated by CH bonds (breaking energy 350 kJ/mol).

The aging behavior of plasma treated polymers, manifested by the trend of the contact angle to recover after treatment is a well known phenomenon [15]. It is caused by the saturation of active sites and migration of the functional groups from surface. The persistence of wettability modification was investigated by measuring the variation of the contact angle after storing long periods of time, and is shown also in Fig. 5. It is important to notice that the recovery is not complete, and the treated materials remain more hydrophilic then the original samples even after 20-30 days, except for PTFE.

3.2.2 AFM investigations

Examples of AFM investigation of surfaces modified by plasma treatment are given in Figs. 6 and 7, for PET and PTFE, respectively. The images were obtained in air and non-contact mode. The images describe the surface topography in three moments: (a) initial surfaces, (b) after $0.2sec/mm^2$, and (c) after $5sec/mm^2$. While for 1 scan the change of surface topography is minor, it is significant after $5sec/mm^2$.

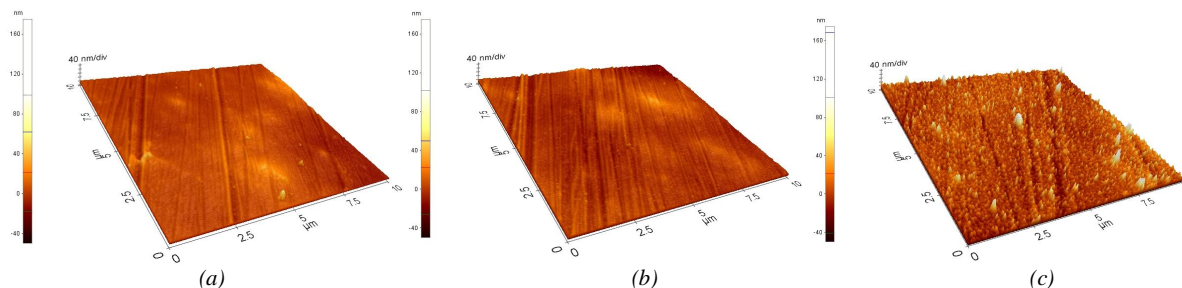*(a)*   *(b)*   *(c)*

Fig. 6. Topography of the PET surface at different moments: (a) initial surfaces (RMS 6.6nm), (b) after $0.2sec/mm^2$ (RMS 7.3nm), and (c) after $5sec/mm^2$ (RMS 14.6nm).

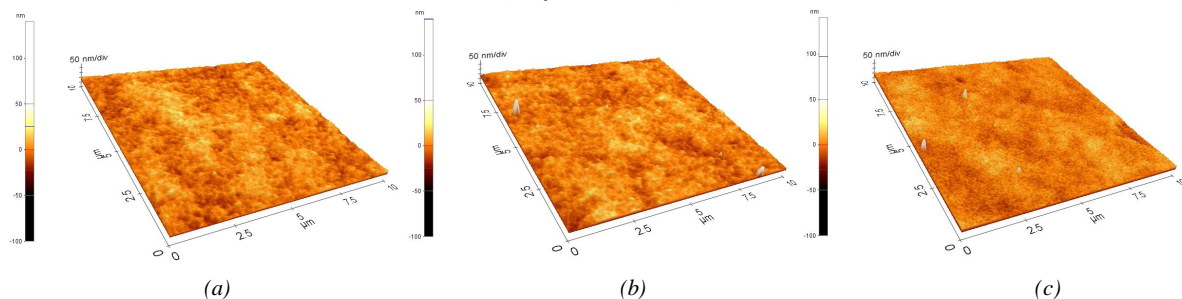*(a)*   *(b)*   *(c)*

Fig. 7. Topography of the PTFE surface at different moments: (a) initial surfaces (RMS 6.7nm), (b) after $0.2sec/mm^2$(RMS 6.3nm), and (c) after $5sec/mm^2$ (RMS 6nm).

The roughening of the surface is proven by the images in Figs. 6 (c) and 7 (c). Chemical etching could be responsible for the roughening, in which carbon atoms from surface are reacting with plasma species leading to volatile compounds [16]. In addition physical sputtering might be important [17]. OES investigations showed the very presence of Ar atomic lines. Many of the radiative transitions in argon end in metastable states: it results that plasma is rich in argon metastables (Ar^m excitation energy ~11.6 eV) which carry out energy at the substrate and may produce physical erosion. As the contact angle change significantly after 1 scan, we conclude that the chemical groups formed at surface is fast and is responsible for the wettability increase in the early stage of the treatments.

3.3 Adhesion tests

The adhesion of plasma samples treated (PET, PE, PTFE and PVC) is considered to be improved if the necessary force for detachment of scotch tape (Scotch 3M1, Magic TM Tape) increase as results of treatment. In Fig. 8 is presented the dependence of the detachment force upon the number of scans. It can be observed that the rate of adhesion increase even after the first scan. The necessary force for detachment of scotch tape treated foils

compared with untreated samples increases after 5sec/mm^2 by 58% for PE, 68% for PET, 69% for PVC, 42% for PTFE.
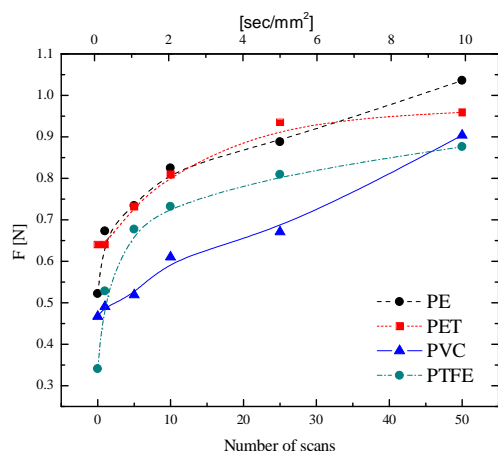

Fig. 8. Dependence of detachment force upon the number of scans (2 mm from nozzle, 4500 sccm, 15 W).

The increase of the detachment force is due both to surface activation by plasma-induced chemistry and to increase in the area of contact with the roughened surface [18].

4. Conclusions

We have presented a radiofrequency plasma source based on a trapezoidal parallel plate dielectric barrier discharge, in which the gas passes through the discharge space and expands from the interelectrodic space in the form of a planar plasma jet.

The operation of the source with argon was demonstrated. Beside the argon lines the spectra emitted by the plasma jet present the signature of chemical species that appeared as a result of the interaction of the argon ions and metastables formed in discharge with the surrounding atmosphere. Excited species such as OH, NH, CN, N$_2$, were identified. These are active species, capable of chemical functionalization of surfaces. Moreover, by using Optical Emission Spectroscopy in correlation with molecular spectra simulation, a low gas temperature was determined, which was also verified by thermocouple measurements. Those peculiarities make possible the modification of thermosensitive substrates, that is useful for applications which require hydrophilic surfaces to interact with other materials. The surface modification was tested for PET, PE, PTFE and PVC polymeric materials. The AFM investigations showed an increase in the roughness of the surface of the treated materials, after scanning with the plasma. The contact angle measurements showed a significant increase of wettability after treatments, lower for PTFE polymer. As o consequence of these changes the adhesion of the respective polymers increased, which was demonstrated by scotch test measurements.

Due to their small size, atmospheric pressure operation, versatility and flexibility the plasma sources of the type described can be further used in specific applications for local surface modification or for processing of complex 3D substrates.

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