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Operations domains of a small size atmospheric pressure cold plasma source and its application to polymer surface modification

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Introduction

Plasma treatments are good alternatives to the chemical methods of modification of surface properties. Such modifications are important for adhesion control and biomedical applications, as example the control of the cell growth. Atmospheric pressure plasma is desirable for such applications in comparison to vacuum treatments. A small size plasma source producing cold plasma is presented, whose operation is based on the expansion of a radiofrequency discharge in argon.

The operation with oxygen or nitrogen is of interest, the atoms and excited states of these gases being known for their chemical activity. Nevertheless, the operation of the source in the cold regime in molecular gases is precluded by the higher energy needed to sustain the discharge. Active species production is possible as well in argon/oxygen and argon/ nitrogen mixtures. The operation domains of the source in the cold regime were established in the power - gas flow rate coordinates for various concentrations of the molecular gases in argon. The stable operation is proved with molecular gases added in small concentrations.

The small size plasma source is used for surface modification by scanning PET, PE and TFTE foils. An important decrease of the contact angle is noticed, strongly dependent on the scanning speed and the number of scans. The effect of mixing the molecular gases to the main gas upon the surface energy was studied.

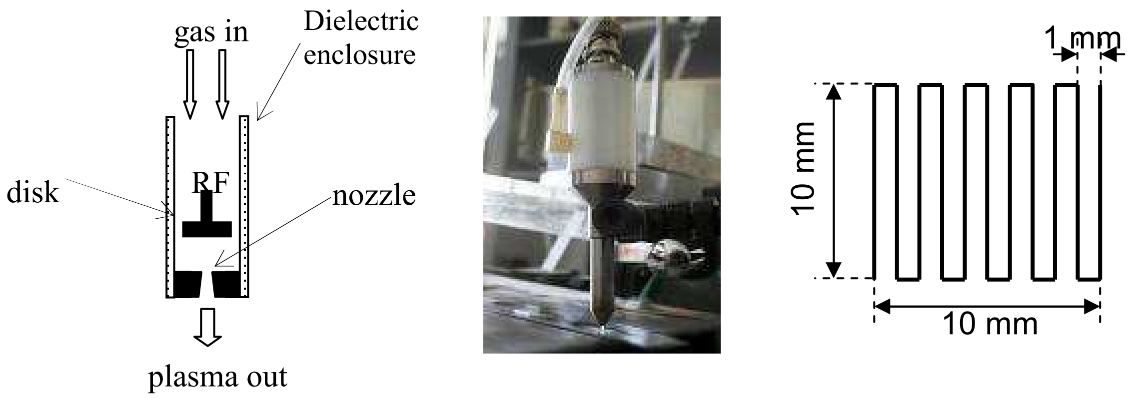
Experimental setup

This plasma source is only 8 mm in diameter, and does not heat significantly the substrate, the temperature of a thermocouple inserted in the plasma beam being in the range 40-80 ^{o}C for forwarded RF powers in the range 12-25 W and mass flow rates in the range of

2-5 10^3 sccm. The plasma was generated at atmospheric pressure by RF capacitive discharge. The experiment consisted in the atmospheric pressure plasma jet scanning of PET, PE and PTFE foils. These polymeric materials are used due to their characteristic properties: mechanical and thermal resistance, etching resistance, low density, low electrical and thermal conductivity, etc.

The basic operating principle is the same as for the higher value radio-frequency power plasma sources [1], the discharge being realized between a RF powered electrode and a nozzle separated by a small gap (Fig.1). To decrease the plasma source's outer dimensions and considering the fact that the operating radio-frequency powers are of low value, the cooling of the electrodes was discarded

PE, PTFE and PET foils of 10 by 30mm have been scanned on a area of 10x10mm with the help of a motorized x-y translation stage with PC interface. The jet's movement above the surface was done at a rate of 5mm per second, equivalent to a 0.2 sec per scanning exposure time. The plasma was generated at atmospheric pressure by RF (13.56 MHz) capacitive discharge.



Schematic view of the plasma source *Image of the plasma source during scanning* *Drawing depicting the path of the scan.*

Fig. 1

The atmospheric pressure plasma jet parameters were: RF power = 14W, gas: Argon, gas flow = 4500 sccm, plasma jet's diameter: 1 mm, substrate-nozzle distance=2mm, gas temperature: 51^0, pressure: atmospheric, no cooling.

Operation domains

In Figure 2 are presented the operation domains of the plasma source in argon-oxygen mixture and argon nitrogen mixture. We have obtained a series of closed curves for each gas mixtures (Fig.2). The left graph presents the operation domains for argon diluted with 3 sccm of nitrogen while the right one the operation domains for argon diluted with 3 sccm of oxygen. It is observed that the operation domain is reduced by the admixture of molecular gases. The operation in oxygen containing gas asks for more RF power.

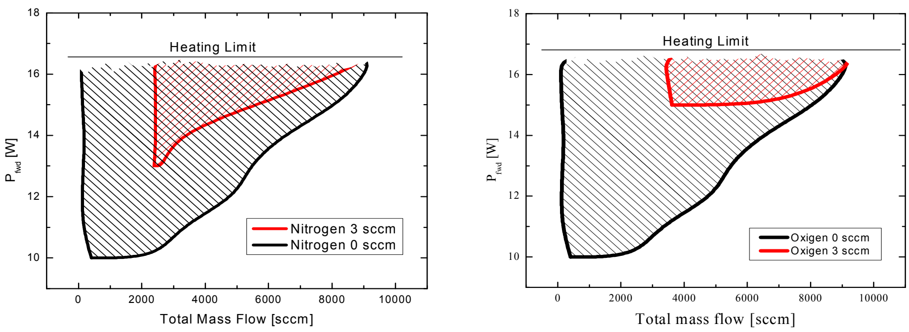


Fig. 2 Operation domains of the atmospheric plasma source for Ar, O_2/Ar, N_2/Ar

Surface modification

The plasma treatments induces important changes on the surface properties of polymers [2]

By Atomic Force Microscopy studies it is shown that, working only in argon, the surface topography is affected for large number of scans, in different ways (Fig. 3).

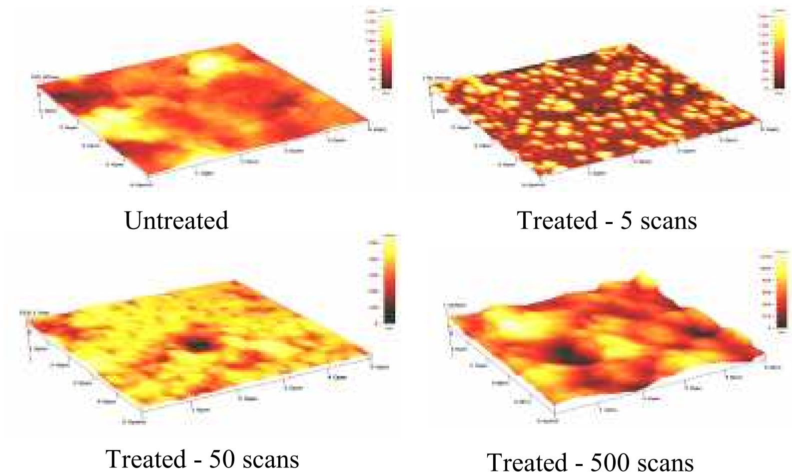


Fig. 3. AFM images of plasma treated PET surfaces

The treated surface (PET) becomes more hydrophilic after successive scans, the contact angle values decreasing from 84^0 to 45^0 (after 50 scans). Similar decreases of the values of the contact angle were observed on other materials such as polyethylene (PE) and polytetrafluoroethylene (PTFE). The use of admixture of oxygen or nitrogen in the working gas greatly favor the hydrophilisation of surface the contact angles changing from 84 to 30 degrees after 50 scans (Figure 4).

Adhesion of the treated surfaces was measured using the set-up depicted below (Figure 5a.) with a Scotch tape from 3M-Scotch®. We have observed that the force necessary for detachment of the tape from untreated / treated polymeric films increases with the number of scans. More precisely, for PET treated with argon plasma the adhesion has increased by 480% compared to the initial value. For PTFE the increase was 533%, while for PE the same increase was 350% (all after 500 scans).

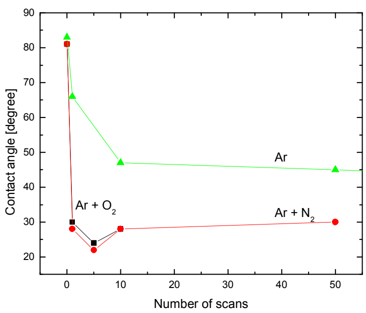
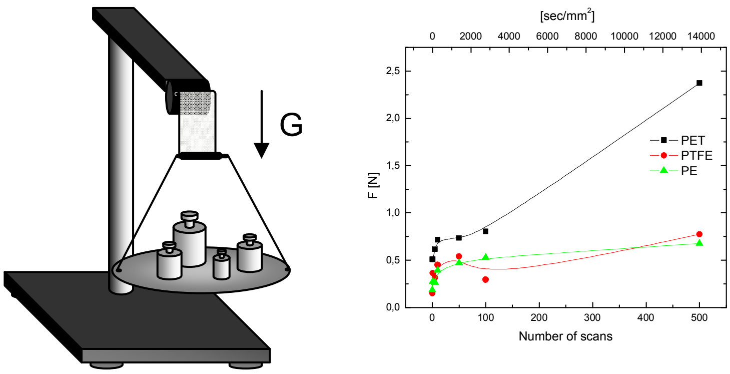


Figure 4. The dependence of the contact angle vs. number of scans. for PET samples treated in Ar, Ar/O2 and Ar/N2 mixtures



a) b)

Figure 5 a) setup for measurement of adhesion, b) dependence of detachment force upon the treatment number of scans.

Conclusions

The operation of an atmospheric plasma source in argon and argon /oxygen or nitrogen admixtures was demonstrated. Polymeric materials (PET, PE and PTFE foils) have been treated with the generated cold plasma jet. The AFM measurements show surface roughening. The roughness depends on the number of scans, and increases considerably at large scanning numbers (more that 50, equivalent treatment time 10 sec/mm^2). The hydrophilic character of the materials (including PTFE) is improved by plasma treatment, in two sequences: a fast decrease at the first scans and a slow decrease after a large number of scans. The adhesion of polymeric treated materials is improved substantially by plasma treatment.

References

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[2] S. Yang, M. C. Gupta, Surface & Coatings Technology 187 (2004) 172-176