

Surface modification of polystyrene beads using RF atmospheric pressure plasma jet

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Abstract: The present work investigates the opportunity of using a cold RF plasma jet generated at atmospheric pressure for surface modification of polymeric materials with complex shapes, focusing on the modification of polystyrene (PS) spherical beads and flat surfaces. An enhanced wettability corroborated to increase in surface roughness and modification of surface chemical composition was demonstrated upon plasma exposure.

Keywords: atmospheric pressure plasma, material processing, wettability, polystyrene beads.

1. Introduction

Polymeric materials are widely used in many applications due to their mechanical properties, (including flexibility) thermal conductivity, transparency, chemical inertness, etc.. Polystyrene (PS) is among the mostly used materials for biomedical applications, as example in the control of cell growth, cell attachment and tissue engineering [1, 2], biocide activity [3], as well as an optical material [4]. However, some applications require certain surface properties (wettability, adhesion, biocompatibility), that can be attained by means of cold plasma treatment [5].

In the present paper, plasma processing of polystyrene beads in a rotating fluidized bed configuration is discussed, focusing on the modifications induced to the surface wettability and chemical composition. Moreover, it is well known that Argon plasma treatment of polymeric surfaces results in improved hydrophilicity and biocompatibility behavior [6, 7].

The samples were characterized by ATR/FTIR, AFM and water contact angle measurements.

2. Experimental procedures

All the plasma treatment experiments have been performed with an atmospheric pressure capacitively coupled RF plasma jet (13.56 MHz) operating in Ar, at various gas flows, in the range 5000 -9000 sccm, using a RF power of 15 W. The operation principle has been described in detail elsewhere [8].

2.1 Fluidization

The fluidization experiments have been performed in open atmosphere, using a cylindrical reactor; of 20mm diameter and 90mm height, which accommodates the PS beads, the RF plasma source and a Teflon adapter between them, in order to

mechanically stabilize the system (Figure 1). Different numbers of spherical polystyrene beads, from 6-12, with a diameter of 6.15mm, were placed in the reactor, according to the available reactor volume. One of the beads was colored, thus allowing its tracking during the movement inside the reactor. Experiments have been performed with an Ar flow of 9000 sccm, corresponding to the minimum flow which allowed the beads

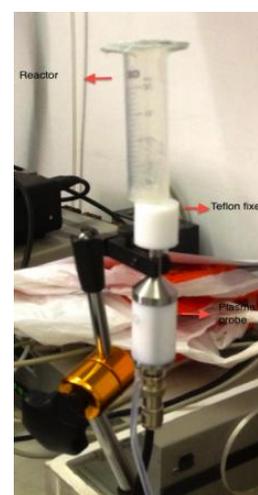


Figure 1. The system used for the fluidization

movement inside the fluidization chamber. A short video (5-10 min) was recorded for each experiment. The number of passes of the colored polystyrene bead in front of the plasma source on every minute of experiment was counted, and the

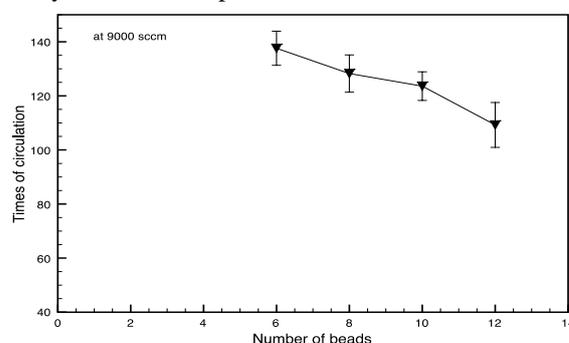


Figure 2. Circulation rate of PS beads depending on the total number of beads in the fluidized bed reactor at 9000 sccm gas flow rate

results were evaluated statistically and presented in Figure 2. It can be seen that the number of recirculation in front of the plasma source decreases as the number of PS beads is augmented; therefore the time of exposure of each PS bead to the plasma source is decreasing, from 0.08 s/mm² (6 beads) to 0.04 s/mm² (12 beads).

2.2. The rotating bead experiment and plasma treatment of polystyrene beads

In order to treat a single PS bead on its entire surface, a specific experiment was designed. The experimental setup comprises the plasma torch in a vertical arrangement with the plasma jet flowing downwards and a copper machined holder in which the PS bead was placed, as illustrated in Figure 3. This set-up allows the free rotation of the PS bead when a gas flow is set through the source, conducting to an uniform treatment of the entire polymeric surface. The distance between the plasma torch nozzle and the PS bead was set to 1 mm. In this configuration, the exposure time per surface unit can be varied by means of total treatment time, which gives an equivalent rate of 0.5 s/mm² for 1 minute exposure.

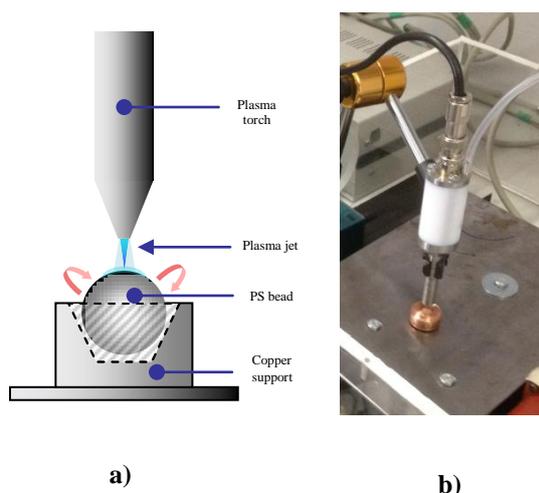


Figure 3. Experimental set-up: a) schematic view and b) image during treatment

2.3. Preparation and treatment of PS flat surfaces

For the treatment of polystyrene flat surfaces, the plasma source was fixed above an X-Y computer controlled scanning stage, as shown in Figure 4. The atmospheric pressure plasma jet parameters were set as follows: RF power of 15 W and Argon flow rate of 5000 sccm. The distance between the nozzle and the substrate was set to 1 mm, which corresponds to an exposure area of 1 mm diameter. Silicon substrates of 10x10 mm² were used to accommodate the PS films, upon cleaning in ultrasonic bath in subsequent steps, with soap, acetone and ethyl alcohol, and dried with nitrogen flow. An automated spin coating instrument was used to obtain polystyrene films from toluene based

solution with a concentration of 14.11 mg/ml. The polystyrene-coated silicon (SiPS) surfaces were placed on the stage and scanned over their entire surface. The scanning route was designed to ensure a quasi-uniform treatment of the surface, with parallel paths spaced at 1 mm distance (Figure 4). The scanning speed was 2 mm/s, which corresponds to a plasma exposure of 0.8 s/mm² along the scanning path.

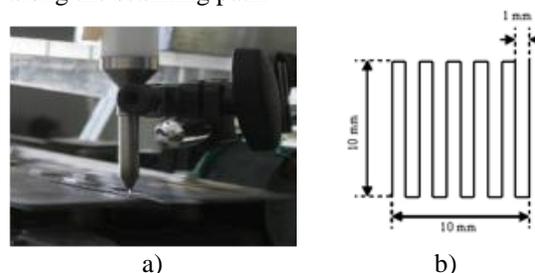


Figure 4. a) Image of the plasma jet source during treatment; b) the scanning path on the sample

The modification of wettability (hydrophilicity) of polymeric films (SiPS) was evaluated by water contact angle measurements, performed by means of a KSV Instrument provided with CAM101 optical system. The static contact angles between the polymeric surface and liquid (distilled water) have been measured after placing 1 μ l water droplet on the surface.

Argon plasma effect on the PS surface topography was investigated by atomic force microscopy (AFM) using a Park Systems, XE-100 model, working in non-contact mode, which allows a maximum scanning area of 50 \times 50 μ m².

Fourier Transform Infrared Spectroscopy spectra were recorded with a JASCO 6300 spectrometer provided with an Attenuated Total Reflectance (FTIR-ATR) module. Measurements have been performed in the spectral range 400-7800 cm⁻¹, with a resolution set to 4 cm⁻¹ and an average number of 1024 scans. The spectra of the treated and untreated samples were compared in order to assess the chemical changes induced by plasma treatment on the polystyrene surface.

3. Results and discussion

3.1. Atomic Force Microscopy studies

The topography of the PS surfaces exposed to plasma is presented in Figure 4. An important roughening effect appears upon the first scan, while only slight modification of the RMS roughness of polystyrene polymeric surfaces is observed when increasing further the number of scans.

Such behavior can be explained by chemical modifications induced on the surface by the active species present in the plasma jet, in conjunction with a surface etching effect predominant upon longer exposure.

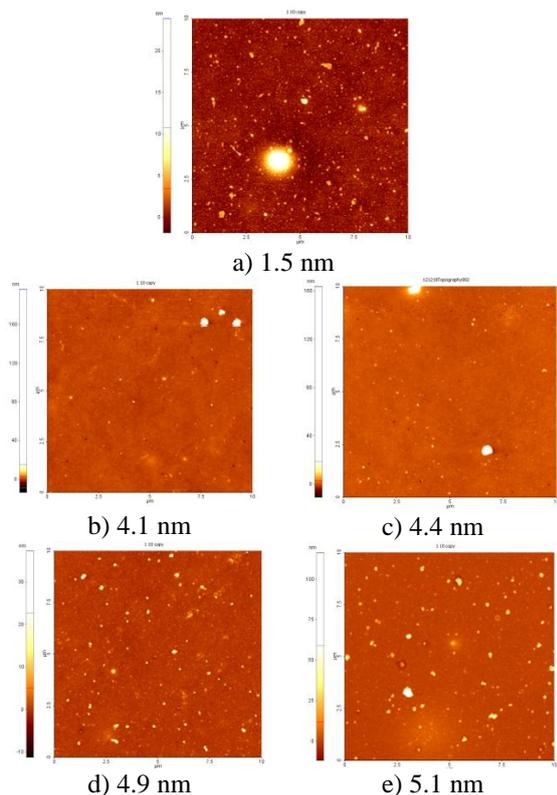


Figure 4. AFM images: a) initial surface b) 1 scan c) 2 scans d) 5 scans and e) 10 scans.

3.2 Modification of wettability

In the case of polystyrene beads, it is difficult to determine their surface wettability in a quantitative manner. Nevertheless, a qualitative assessment of conducted by placing an untreated and a plasma wettability enhancement upon treatment has been treated PS bead ($5\text{s}/\text{mm}^2$) on a microscopic slide covered with 0.7 ml distilled water. The optical images of water behavior on both beads are presented in Figure 5. They evidence a higher water contact area for the plasma treated material, pointing out toward a more hydrophilic behavior of the surface.



Figure 5. Images of PS beads (a) untreated and (b) plasma treated for $5\text{s}/\text{mm}^2$

Quantitative assessment of the wettability enhancement induced by plasma treatment was performed on polystyrene flat surfaces, by means of contact angle measurements. In Figure 6 is presented the variation of the contact angles with the number of scans performed on polystyrene

films, in conjunction with the evolution of the surface RMS as resulted from AFM measurements. A significant decrease of the contact angle is encountered even at low exposure time of $0.8\text{ s}/\text{mm}^2$, corresponding to only 1 scan, while slower decrease is encountered upon increasing further the exposure time (through the number of scans). The value of the contact angle for untreated samples of SiPS was 81° , proving a rather hydrophobic character. Even after the first scan, the contact

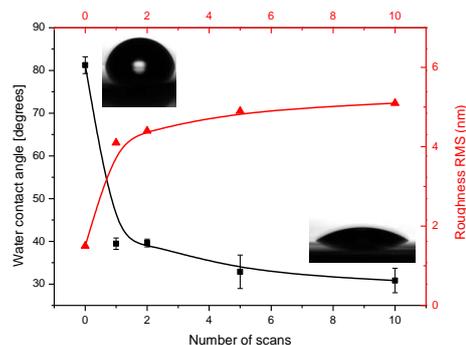


Figure 5. The dependence of PS water contact angle and roughness RMS upon the number of scans

angle decreased from 81° to 39° and a constant value of $\sim 30^\circ$ was obtained after 5 and 10 scans. As a result, plasma treatment obviously leads to a decrease of the water contact angle of the surfaces, showing an increase of the surface hydrophilicity, in correlation to an enhanced surface roughness.

3.3. Chemical composition

To assess the possible changes in terms of chemical structure of polystyrene surfaces, ATR-FTIR spectra were recorded. These spectra were acquired before and after treatment of the polystyrene films in plasma. Figure 8 shows the ATR-FTIR normalized spectrum in the wavenumber region from 1000 to 3500 cm^{-1} . Untreated polystyrene spectrum shows the prominent vibration bands specific to aromatic vibrations of C-H bonds in the range 3001 - 3103 cm^{-1} , the C-C in plane stretching vibration of ring at 1601 cm^{-1} , C-H stretching and C-H bending in plane ring vibrations at 1493 cm^{-1} and respectively at 1028 cm^{-1} . The aliphatic bond vibrations are present through the CH_2 asymmetric and symmetric stretching vibration at 2924 cm^{-1} and respectively 2850 cm^{-1} , while the band at 1452 cm^{-1} associates to the C-H deformation of CH_2 [9]. Following the argon plasma treatment, significant modifications in the ATR-FTIR spectra are observed, namely an overall decrease of the aromatic ring vibrations associated to the appearance of CH_3 asymmetric and symmetric stretching vibration at 2958 cm^{-1} and respectively 2872 cm^{-1} . Such behavior could be explained by the destruction of the aromatic structure on the surface level followed by rearrangement of

polymeric chain. The most significant change is represented by the appearance of the peak at 1726 cm^{-1} which can be attributed to the formation of carbonyl group (C=O), which is responsible for the hydrophilic behavior of the PS surfaces after the argon plasma treatment.

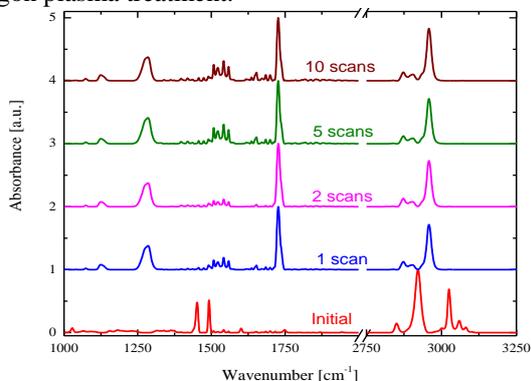


Figure 8. ATR-FTIR spectra of initial PS films, and plasma treated PS films for various numbers of scans

4. Conclusion

Spherical beads and flat films of polystyrene were treated in argon plasma using a cold RF plasma jet source generated at atmospheric pressure, based on a discharge with bare electrodes. The results proved an enhanced wettability effect induced on the polymeric surfaces, in connection to an increased surface roughness. The ATR FTIR study showed the modification of the chemical composition through the partial destruction of aromatic bonds and the appearance of C=O functional group. These results open up new possibilities regarding the plasma treatment of objects with large and complex shapes, as those

provided by the food industry, e.g. almonds, nuts, etc.

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