# PROCESSING OF POLYVINYL CHLORIDE SURFACES WITH ATMOSPHERIC PRESSURE DIELECTRIC BARRIER DISCHARGES FOR UROLOGY APPLICATIONS

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*Abstract*. Plates and films prepared from PVC material used in medical applications were exposed to a cold argon plasma jet generated by a dielectric barrier discharge at atmospheric pressure aiming to produce surface hydrophilization. Water contact angle decrease was significant for both sample types surface, with only small changes in surface roughness at low exposure times. Moreover, the modified films were less prone to hydrophobic recovery than plates. An innovative dielectric barrier discharge concept for in line processing the outer surface of objects with complex shape such as catheters is presented.

*Key words*: hydrophilicity, surface processing, atmospheric pressure plasma, polyvinyl chloride, argon discharge, catheter.

## 1. INTRODUCTION

Urinary catheters are indicated to be used in patients with urological problems such as chronic urinary incontinence and retention, as well as for the measurement of the bladder residual volume, obtaining uncontaminated urine for microscopy and culture, intravesical installation of drugs, urodynamic assessment and the treatment of acute urinary retention [1,2]. Beside the clinical effectiveness of catheters, induced complications are often associated with urinary catheterization such as patient discomfort, irritation, inflammation [3,4], urinary tract infection, mechanical trauma [5], urethral fistulae [6], urethral stenosis and stricture [7], and urosepsis [8]. Studies have shown that the catheter complications could be related to various aspects of catheter design such as material composition, coatings, shape and physical properties. Regarding the material surface properties, hydrophilic coated catheters which interact with water to produce gel-like substances may facilitate the insertion of the catheter into the urethra and reduce the incidence of tissue damage and discomfort [9]. These coatings have some drawbacks, being susceptible to wear with repeated use and become sticky if inserted over extended periods of time [10]. Other techniques were proposed for surface hydrophilization such as high-energy irradiation [11], ultraviolet [12], ozone [13] or by wet chemical means [14]. Among mentioned techniques, the cold plasma technique is extensively used to engineer the polymer surface in a controlled and efficient manner, rendering it hydrophilic while the bulk properties (mechanical resistance and flexibility) are retained and the costs reduced [15,16]. As already known, the induced modifications by plasma are in principle attributed to chemical and morphological changes. Hydrophobic to hydrophilic surfaces were created using argon plasma immersion ion implantation due to oxygen incorporation [17] and by adjusting the power levels in RF plasma treatments [18].

The first part of this paper contains results about the surface properties modification of medical *polyvinyl chloride* (PVC) using an atmospheric pressure argon plasma source based on a dielectric *barrier discharge* (DBD) configuration. The main advantages of utilizing a DBD are the high efficiency and flexibility with respect to its geometry and electrode configuration, size requirements ranging from a few millimeters to meters, type of materials to be treated, working gas mixtures used to treat or to coat the material surface [19,20]. As substrate models for experiments, two types of PVC were proposed – film and plate, both being used for manufacturing intermittent Foley catheters. Typically, urinary catheters are made of different materials (latex, silicone rubber, PVC or teflon) and types (Foley catheter, straight catheter or curved catheter) with diameters within the range of 1–2 mm, whereas the tube length is mostly longer than 400 mm. Several developments of DBD sources were dedicated for the inner treatment of long flexible tubes, ranging from the ignition of plasma by means of an outer and an inner-tube electrode up to the usage of afterglow plasmas or plasma bullets [21–23] as well as for the outer surfaces of tubes and other hollow dielectric bodies using liquid electrodes for plasma generation [24]. In the second part of this paper, we introduce an innovative DBD based concept for the processing of outer surface of small diameters tubes made of medical PVC.

## 2. MATERIALS AND METHODS

### 2.1. MATERIALS

Two types of PVC (plate and film) with similar composition (granules of PVC S 170100, DEHP [di-(2-ethylhexyl) phthalate], epoxidase soya bean oil and stabilizer (Baerostab 170)) were used in this study. PVC plates (500 µm in thickness) were acquired by pressing the granules for 10 min at 165 $^{o}$C and 220 bar pressure using a Brabender Polystat T200 press apparatus. PVC films (100 µm in thickness) were obtained by dissolving the granules in cyclohexanone using an AREC magnetic stirrer at 110$^{o}$C and 600 rpm for 5 hours. Cyclohexanone is an organic solvent used in the production of PVC medical devices, including intravenous fluid bags and extracorporeal circulation circuits [25].

### 2.2. PLASMA TREATMENT

Plasma treatments were performed with an atmospheric pressure DBD source with an integrated motorized scanning stage integrated, which is described in [26]. The DBD is based on a plan-parallel discharge with a single dielectric barrier, which defines together with the ground electrode and the lateral spacers a trapezoidal discharge volume, which has the role in focusing the plasma outside the interelectrodic space (Fig. 1). Surface processing was carried out using: an RF power of 14 W, gas argon, a gas flow of 4500 sccm, a plasma jet diameter of 1 mm, a nozzle-substrate distance of 2 mm, at atmospheric pressure.

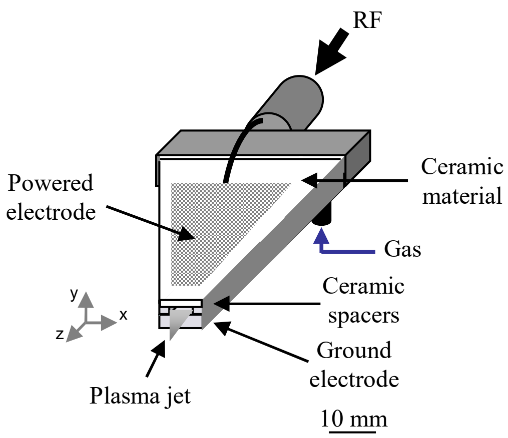


Fig. 1 – Schematic diagram of the plasma source with a single barrier and trapezoidal parallel configuration.

The PVC samples were exposed to the Ar plasma using a scanning procedure, which allowed for a uniform surface modification. The motorized scanning stage with computer control movement in $x - y$ coordinates used a route consisting of parallel paths at 1 mm distance. The scanning speed was 2 mm/s, which correspond to an exposure of 0.8 s/mm (80 s for 10 mm × 10 mm surface) along the scanning path.

### 2.3. PLASMA CHARACTERIZATION

*Optical emission spectroscopy* (OES) measurements were conducted using a 0.5 m Bruker Spectrograph with Andor IDus CCD camera and an optical system for collecting the light. The imaging mode was utilized: the spectra along the flowing direction (z-axis) of the jet were recorded (in the spectral range 200–1100 nm) on the CCD all at once, by projecting the central part of the jet (extended along the z direction) on the height of the spectrograph slit height.

### 2.4. SURFACE CHARACTERIZATION

Static contact angle measurements were performed under ambient air at room temperature by the sessile drop method using a KSV 100 contact angle analyzer. Drops of distilled water with defined volume (0.5 μl) were deposited on polymer surface with a microsyringe. The aging studies were carry out by measuring the contact angle as a function of storage time of plasma treated samples at room temperature. Three contact angle values were measured over an extended area for each treated sample to calculate the averages and standard deviations.

*Atomic force microscopy* (AFM) analyses were carried out using a Park Systems XE-100 AFM (DE) with Nomad equipment operated in non-contact mode. Surface images for quantitative analysis were obtained from $40 \times 40$ $\mu m^2$ scales at a resolution of $256 \times 256$ pixels.

## 3. RESULTS AND DISCUSSION

### 3.1. PLASMA CHARACTERIZATION

The plasma source used in this study is a DBD plasma jet generated in argon and expanding in the open atmosphere. Therefore, the plasma chemistry is affected by the ambient air chemistry resulting in a mixture of argon, nitrogen and oxygen [27]. The spectral characteristics of the argon discharge recorded at the nozzle exit (0 mm) and at 2 mm distance from it, are presented in Fig. 2 [28]. At the nozzle exit, the emission spectrum dominated by the atomic lines of argon (between 670 nm and 850 nm). In addition, the oxygen spectral triplets from 3s–3p transition [29]: $^5S_1^o - {}^5P_{3,2,1}$ (777.19 nm, 777.41 nm and 777.53 nm) and $^3S_1^o - {}^3P_{2,1,0}$ (844.62 nm, 844.63 nm and 844.67 nm) were observed. Furthermore, emission lines of the *second positive system* (SPS) of molecular $N_2$ at 337.14 nm [30] ($C^3\Pi_u \rightarrow B^3\Pi_g$, $\upsilon' = 0 - \upsilon'' = 0$), first negative system (FNS) of $N_2^+$ at 391.44 nm [31] ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$, $\upsilon' = 0 - \upsilon'' = 0$) and OH at 308.9 nm were identified in the UV range (240–400 nm). The OH radical was probably formed from water vapors present in the ambient air [32]. The estimated argon gas temperature, obtained from fitting the rotational bands of OH ($A^2\Sigma^+ \rightarrow X^2\Pi$, with the band maximum at 308.9 nm), was about 390 K [26].

The distance from nozzle played an important role in the spectral distribution of the plasma species. At 2 mm distance, the atomic lines were almost washed out and the spectrum is dominated by the molecular species emission. This behavior was confirmed by the dependence of the emitted lines and bands intensity upon distance from nozzle (Fig. 3).

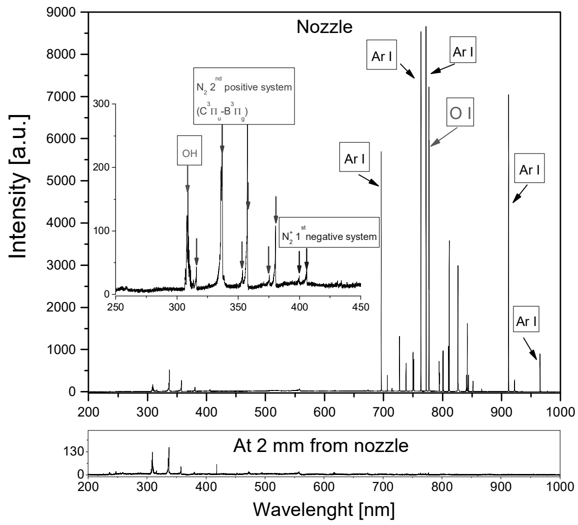


Fig. 2 – Spectra of plasma at nozzle exit (up) and 2 mm far from nozzle (down), at 14 W forwarded power and 4500 sccm argon flow rate.

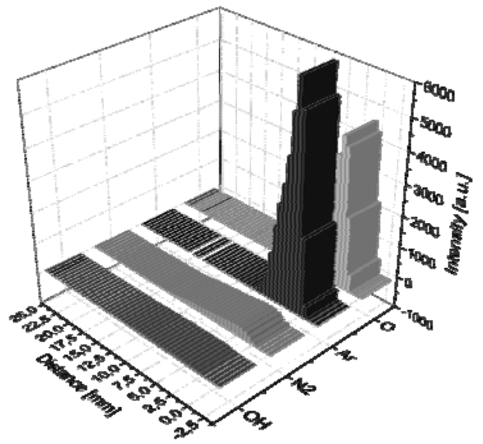


Fig. 3 – Intensity distribution of the investigated species related to the jet nozzle distance.

3.2. SURFACE INVESTIGATION

Untreated PVC is a hydrophobic polymer with a contact angle ~83°. Figure 4 shows the evolution of water contact angle on PVC plate and film as a function of scan number or treatment duration. In both cases, plasma treatment renders the initially hydrophobic surface into a hydrophilic one after 1 scan. The surface hydrophilicity showed a strong dependence on the plasma treating time, the lowest of the contact angle was obtained by scanning the polymer 10 times. The main processes responsible for surface modification of polymers by plasma generated at atmospheric pressure are hydrogen abstraction, surface etching and incorporation of polar groups [33, 34]. According to OES results, short-living active species, such as atomic oxygen and OH radical were identified, which may interact with polymer surface leading to an enhanced hydrophilicity. Due their short lifetime in plasma, the highly reactive species are necessary to be produce immediately at the surface to be treated. Another possibility for surface processing is the interaction of surface with long-living oxygen active species such as ozone produced by argon plasma at atmospheric pressure. Due to its long lifetime, ozone could enhance the surface hydrophilicity even at larger distances (~ cm) between nozzle and substrate where the short-living active species recombined before reaching the polymer surface [33]. At 2 mm distance from nozzle, plasma jet visually touched the PVC surface and therefore one can conclude that short-living species are expected to produce the major changes in the surface hydrophilicity. It was already shown that the atomic oxygen can actually spread up to 2.0–2.5 mm way from the plasma column [34]. Also, the plasma source produces significant UV radiation. So, we checked if UV radiation is responsible for the change of the surface properties and changes of the water contact angle. To verify this, we placed a quartz glass which blocks the species but is UV transparent over the polymer surface, then exposed the sample for 30 minutes to the plasma source. There was no change in the water contact angle. Regardless of the polymer type, the PVC plate treated with argon plasma had smaller contact angles than the PVC film. After 10 plasma scans, the PVC plate had a contact angle of 38$^o$ while PVC film a contact angle of 50$^o$. This indicated that the cyclohexanone used to dissolve granules and obtain PVC film could affect the degree of polymer surface wetting induced *via* plasma treatment.

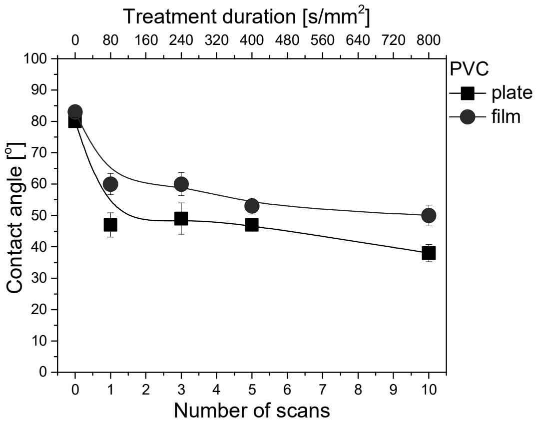


Fig. 4 – Water contact angle dependence for PVC plate and film upon the number of scans (bottom horizontal axis) or treatment duration (upper horizontal axis) with plasma source.

Surface hydrophilization of polymers occurs not only during the plasma processing, but also afterwards, when any radicals that remain on the treated surface can react with ambient air resulting in further incorporation of oxygen functionalities. Nevertheless, by further exposing the plasma treated surfaces to ambient air, an aging process takes place that results in a gradual decline of the prior incorporated functionalities through diffusion of those from the outermost layer to the bulk or by oxidation processes [37]. This thermodynamically driven mobility of functional groups is also called "hydrophobic recovery" that leads to partially or completely loss of incorporated functionalities after a period of time [17, 38].

Figures 5a and 5b display the variation of water contact angle on plasma treated PVC plate and film stored in ambient air for 16 days. The treated surfaces underwent a hydrophobic recovery as reflected by the increasing water contact angle value over time, which is dependent on the scan number. The increase of the contact angle with increasing exposure time is more pronounced for plasma treated PVC plates comparing to treated films. Nevertheless, the treated polymer never recovered its initial hydrophobicity.

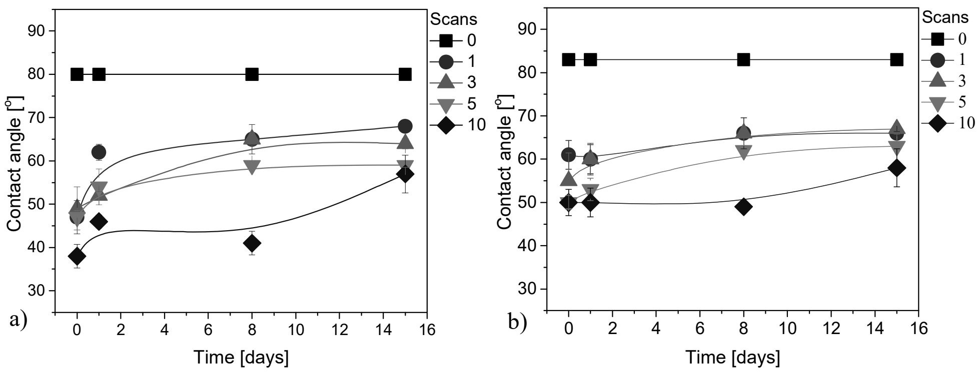


Fig. 5 – Aging behavior of plasma treated PVC a) plate and b) film.

The change in surface topography of PVC plate with respect to number of plasma scans is shown by selected representative 40 x 40 µm 3-D AFM images in Fig. 6. The surface topography of untreated PVC plate is characterized by a uniform surface with some defects, voids and cracks, resulted from manufacturing process (Fig. 6a). After 5 scans (Fig. 6b) and 10 scans (Fig. 6c) PVC plates exhibited changes in topography characterized by the appearance of a multitude of nanostructures and grains on the surface. These changes in the surface topography could be attributed to etching by reactive species. In reaction with the ambient air, the ionized argon atoms from the DBD discharge, and also possible the argon metastables, created reactive species that can etch the polymer and roughen its surface.

PVC film surfaces exposed to plasma showed no significant topographical changes, the voids and cracks on the particular surface of untreated PVC film (Fig. 7a) resulted from the manufacturing process are still visible after 5 scans (Fig. 7b), only few grains appeared at the surface after 10 scans treatment with plasma (Fig. 7c). In this case no etching process occurred. Comparing the topography of PVC plate treated by plasma with the one of treated film, the differences were noticeable: the plate surface was characterized by a multitude of grains; the initial surface of untreated plate was not recognizable anymore while plasma treatment induced no significant changes on the topography of the film surface. Consequently, the etching process depends on the characteristics of the material to be etched.

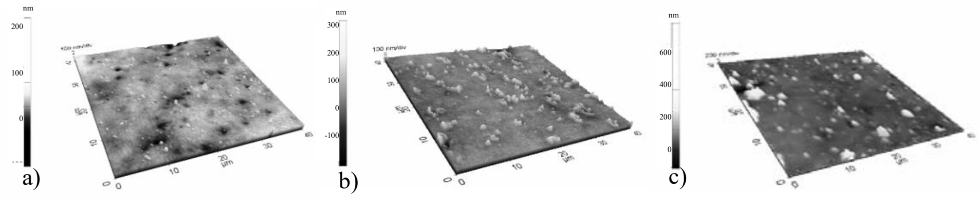


Fig. 6 – 40 × 40 µm AFM images (3-D) of PVC plate: a) untreated and treated with plasma; b) 5 scans and c) 10 scans.

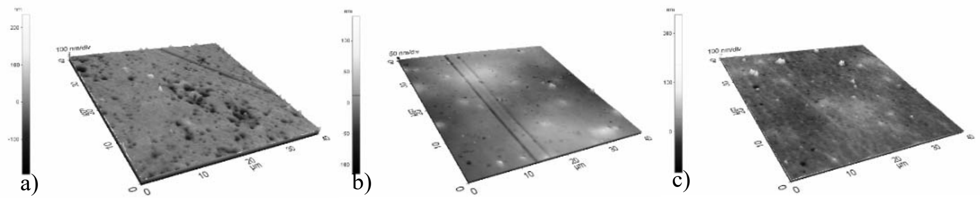


Fig. 7 – 40 × 40 µm AFM images (3-D) of PVC film: a) untreated and treated with plasma; b) 5 scans and c) 10 scans.

The values of determined root mean square roughness ($R_{rms}$) varied between 15–76 nm for PVC plate and 13–23 nm for film, depending on the treatment time (Fig. 8). It was found that the surface roughening leads to the change of the polymer's wetting characteristics when $R_{rms}$ has a value larger than 100 nm [39]. Therefore, the considerable decrease of the water contact angle with increasing plasma scan number could be attributed to the insertion of polar functionalities on polymer surface [40] and not to changes in surface roughness.

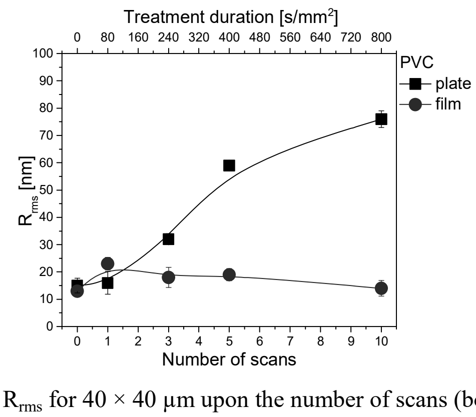


Fig. 8 – Dependence of $R_{rms}$ for 40 × 40 µm upon the number of scans (bottom horizontal axis) or treatment duration (upper horizontal axis) with plasma source.

### 3.3. DISCHARGE CONFIGURATION SUITABLE FOR PLASMA PROCESSING OF OUTER SURFACES OF TUBES WITH SMALL DIAMETERS

Modification of outer or inner surface of polymeric objects with complex geometry such as catheters requires particular plasma devices. In this respect, an atmospheric pressure plasma set-up based on dielectric barrier configuration that allows treatment of outer surface of objects with small diameters was developed [41]. The configuration presented in Fig. 9 uses metallic electrodes of an annular shape placed outside the tube. One is the ground electrode while the other is the power one; their configuration can be altered according to the application, one configuration including a multitude of alternating electrodes being placed along the larger discharge tubes. Plasma is generated inside the tube through a gas inlet placed roughly in the middle of the tube, at atmospheric pressure, using argon as for discharge gas, with gas flows of 1.5 l/min to 6 l/min. The breakdown and maintaining of the discharge is accomplished using RF (13.56 MHz) applied *via* an RF generator and associated matching box.

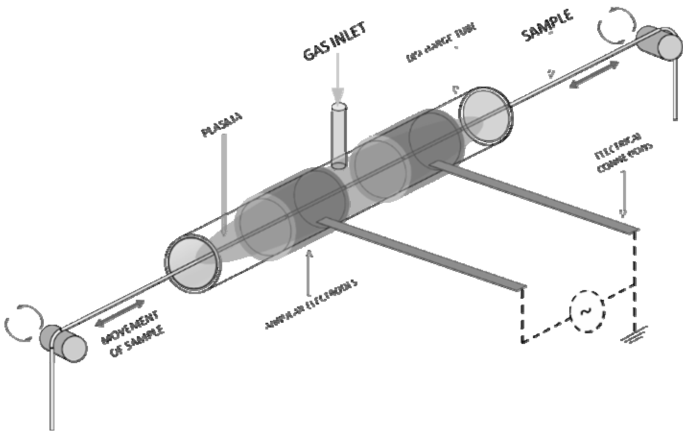


Fig. 9 – Plasma device for processing of outer surfaces of objects with small diameters.

The plasma device setup is variable in terms of geometry, materials and process parameters. The device could be scaled up to 200–300 mm length with the inner diameter ranging from 2 to 8 mm and the outer diameter up to 10 mm. The plasma generated inside the device is rather cold (450–600 K). The object to be treated can be translated through the discharge space using rolling elements coupled to stepper motors. The movement rate of the object inside the discharge space can be varied, from 5 mm/s to 30 mm/s, thus enabling the selection of the treatment time by selecting the appropriate speed. Plasma species generated in the above discharge modify the surface properties, as example changing them from hydrophobic to hydrophilic or in case of using gaseous precursors produce a coating with desired properties (antimicrobial, drug releasing layer, etc.) on the material surface.

## 4. CONCLUSIONS

Polyvinyl chloride plates and films with the same composition but obtained using two different procedures, were subjected to plasma processing using a dielectric barrier discharge generated in argon at atmospheric pressure for surface processing. Regardless of material background, plasma treatments produced hydrophilic and stable surfaces, and preserved the polymer morphology. It should be noted that the hydrophobic recovery and roughness of film treated samples were much lower compared to plate treated samples suggesting an influence of using cyclohexanone in preparation procedure of films. Nevertheless, the surface hydrophilization and the minimal surface roughening induced by plasma, are linked to the unique properties of the argon discharge. It was shown that the dominant emission of atomic species compared to the molecular ones changes into the dominance of emission from molecular species with increasing the distance from nozzle. Most probable this is due to the lower excitation energy of levels in molecules. In addition, an innovative configuration of DBD suitable for treatment of outer surface of tubes of small diameters was introduced. According to the results of this study, the choice of using DBDs for processing flat or convex polymeric surfaces with applications in the field of urology is of great importance.

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