



Surface modification of polymethylmethacrylate foils using an atmospheric pressure plasma jet in presence of water vapors



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ABSTRACT

In this work polymethylmethacrylate foil surfaces are modified using a non-thermal atmospheric pressure plasma jet generated by a discharge with bare electrodes. The study focuses on a comparison of the treatments performed using plasma generated in Ar/water vapors mixture (humid plasma) and dry Ar. Injecting small amounts of water vapors in the discharge, a substantial improvement of the polymeric foils surface wettability was obtained. For a similar improvement of the wettability, the duration of treatment with dry argon plasma is six times longer. The investigations of the treated surfaces show that the wettability of the polymeric foils is mainly improved due to the surface roughening during dry plasma treatments, while the chemical changes of the sample surface prevail in the case of humid plasma treatments.

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1. Introduction

Due to its properties, polymethylmethacrylate (PMMA) is the polymer of choice for many domestic, industrial and even medical applications. Such as it is, PMMA is transparent, with good resistance at direct sun exposure and ultraviolet light (UV), exhibits low moisture and water absorption, presents good mechanical properties (high mechanical strength, it does not shatter at rupture and it is scratch resistant) and it has a low cost [1]. Similar to other polymers, the main drawback of PMMA is its low surface free energy, leading to poor hydrophilicity and adhesion. These properties can be substantially improved using different techniques for polymer surface modifications, including treatments with wet chemicals [2], UV irradiation accompanied by ozone exposure [3], laser alteration [4] and low temperature plasma at low [5,6] or atmospheric pressure [7–9]. In particular, the PMMA surfaces are dominated by very stable ester methyl groups [10,11], limiting the efficiency of the standard chemical modification procedures [12]; still, plasma treatments of PMMA are more efficient. A literature inspection reveals many studies dedicated to PMMA surfaces treatment using plasma generated in different types of gases: argon, neon, xenon [13, 14], helium [15], oxygen [14,16], nitrogen [17,18], ammonia [19], carbon dioxide [20], air [18,21] and even water vapors containing plasma [12,20,22–26]. Only few of these studies (the most recent ones) are performed at atmospheric pressure [13,15,18,26]. From all

the mentioned feeding gases, water vapor based plasmas are mentioned in literature to be more advantageous when compared to other types of plasma due to high chemical reactivity of hydroxyl groups in respect to ester methyl groups from the PMMA surfaces [12]. In the present paper, we report our results regarding PMMA foils surface modifications using an atmospheric pressure plasma jet, operated either with humid or dry Ar. The treatments were performed for different amounts of humid argon injected in the discharge and the effects over the discharge characteristics and the material properties of the treated PMMA surfaces were assessed.

2. Experimental Details

The experimental setup used for the treatment of the polymeric foils with either dry or humid Ar is presented in Fig. 1. It consists of three main parts: the atmospheric pressure plasma jet (APPJ) source, the gas feeding system and the scanning system.

The APPJ is based on a discharge with bare electrodes (DBE); its operation details were described elsewhere [27]. The plasma source presents a coaxial design and consists in a central metallic electrode, surrounded by an internal ceramic insulator and an external grounded metallic electrode envelope, the last one ending in a conical nozzle. The feeding gas flows along the gap delimited between the central electrode and the ceramic insulator, and the discharge is generated in the space between the central electrode and the conical nozzle using a 13.56 MHz radiofrequency (RF) power supply. Due to the gas flow, the ionized gas expands remotely as a plasma jet with dimensions

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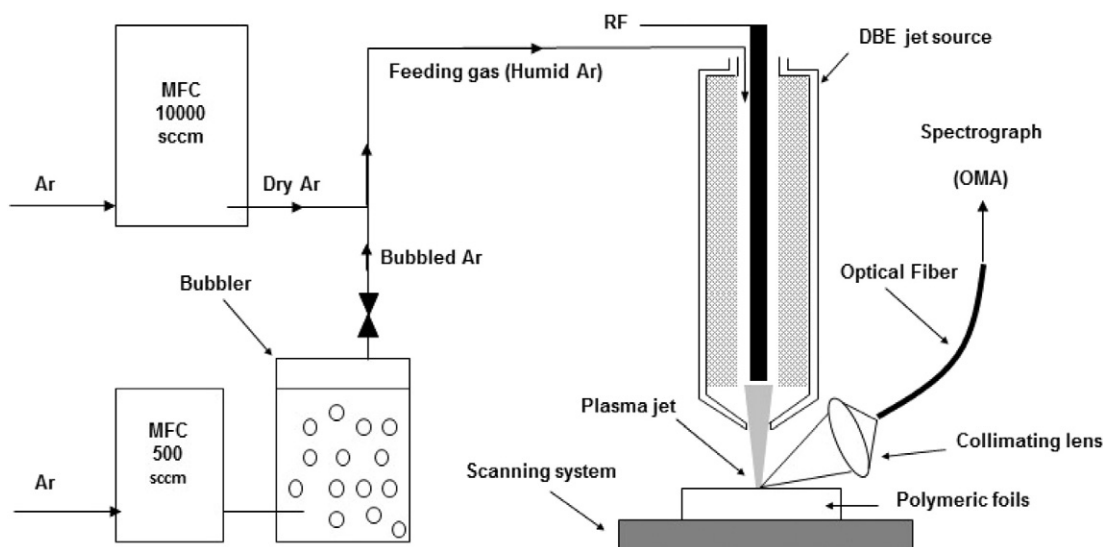


Fig. 1. The schematic diagram of the experimental setup used for treatment of the polymeric surfaces.

depending on the working parameters (for example around 1 mm in diameter and 5 mm length when operated at 4000 sccm mass flow rate of Ar and 14 W of RF power). The working gas is Ar (99.9999% purity) with low content of water as impurity (<1 ppm); it was considered as dry Ar in our experiment. Humid Ar was obtained by passing a stream of dry Ar through a bubbler containing double distilled water. Prior to injection in the plasma source, the humid and dry Ar streams are mixed. The Ar mass flow rates are adjusted using two mass flow controllers (with maximum ranges of 10000 sccm for dry Ar and 500 sccm for humid Ar). The mass flow rate of the feeding gas was 8000 sccm, its water content being varied by adjusting the mass flow of the bubbled Ar between 0 and 400 sccm with steps of 50 sccm (corresponding to a content of humid Ar in between 0% and 5%, with steps of 0.625%).

The treated materials are 500 μm thick PMMA foils commercially available (Goodfellow Ltd.). The treatment procedure is similar with that presented by us in previous works [28] and consists in exposure to the plasma jet of the polymeric foils placed on an x–y translation stage. All samples were treated over a surface of 35 mm \times 35 mm following a parallel lines scanning pattern, the duration of a complete scan being 10 min. Treatments with humid Ar jet were performed for the minimum duration (1 scan), while the dry plasma jet treatments were performed increasing the duration of plasma exposure (i.e. 1, 2, 6 and 10 scans). During all treatments, the distance between the polymeric foil and the plasma source nozzle was kept at 2 mm, while the applied RF power was 14 W.

The spectral investigation of the plasma jet was performed using an optical multichannel analyzer (model HR4000, Ocean Optics) with a spectral resolution of 0.2 nm. The optical radiation was collected from the treatment region using a collimating lens.

The sample temperature during treatment was evaluated in advance as follows. A temperature sensor with thermal characteristics close to that of the PMMA polymeric sample was placed on the substrate holder. The sensor consists in two self-adhesive polyimide very thin foils covering a planar winding of solid platinum wire (actually a Resistance Temperature Detector – RTD sensor). The dimensions of the sensor active area are 20 mm \times 30 mm \times 0.3 mm and its measuring range is in between -80 and $+180^\circ\text{C}$. For temperature evaluation, the sensor was scanned with the plasma jet using the same experimental method used during the PMMA foil treatments. Because PMMA and polyimide have near similar thermal properties [1], the temperatures measured by using the planar RTD sensor are close to that reached by the PMMA foils during their treatment.

The wettability of the PMMA foils was evaluated by static contact angle (WCA) measurements; these were performed by sessile drop method using droplets (1 μL volume) of distilled water in room environment. The WCA values were measured using a computer controlled CAM 101 (KSV Instrument Ltd.) contact angle meter. Each WCA value reported in this work represents the average of six similar measurements.

The topography and the roughness of the PMMA surfaces were evaluated by atomic force microscopy (AFM) using a Park Systems XE-100 instrument operated in non-contact mode; the scan size was 5 μm \times 5 μm . The surfaces morphology was obtained using an FEI S Inspect Scanning Electron Microscope (SEM) with an acceleration voltage of 5 kV; prior the SEM investigations, the polymeric surfaces were covered with a 20 nm thin gold layer for avoiding the electrostatic charging. The chemical composition was studied by ATR-FTIR (Attenuated Total Reflection Fourier Transform Infrared spectroscopy) using a PIKE Technologies Horizontal ATR ZnSe crystal, mounted on a Jasco spectrometer model FT/IR 6300. Each spectrum was obtained by accumulation of 256 scans in the spectral range 600–4000 cm^{-1} with a spectral resolution of 4 cm^{-1} .

All the samples were investigated using the above mentioned techniques. Still, the obtained results are presented only for the samples showing the optimal modification of the WCA after plasma treatment, in comparison with the untreated sample. These samples are denoted with PMMA-D (treatment in dry Ar plasma), PMMA-H (treatment in humid Ar plasma) and REF (untreated).

3. Results

3.1. Optical Emission Spectroscopy (OES) Measurements

In Fig. 2a are presented the OES spectra of the atmospheric pressure plasma jet in the spectral range 200–1000 nm, recorded in the treatment region (i.e. at 2 mm from the nozzle). In both spectra is identified the emission of the following species: OH radical bands in the range 280–309 nm (transition $A^2\Sigma^+ - X^2\Pi$), of N_2 (C-B) second positive system (SPS) in the range 300–450 nm and the atomic Ar I (transitions between the excited levels 1s–2p of atomic Ar) lines in the range 696–1000 nm and the atomic O I (triplet line transitions 3s–3p) at 777.4 nm.

A significant modification of the optical emission spectra is observed (see Fig. 2a) when water vapors are introduced in the discharge: an increase of the OH band intensity, accompanied by the decrease of the atomic species (Ar I and O I) emission is noted. Dependence of the OH,

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