

# Surface modification of polymeric materials by cold atmospheric plasma jet



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## ABSTRACT

In this work we report the surface modification of different engineering polymers, such as, polyethylene terephthalate (PET), polyethylene (PE) and polypropylene (PP) by an atmospheric pressure plasma jet (APPJ). It was operated with Ar gas using 10 kV, 37 kHz, sine wave as an excitation source. The aim of this study is to determine the optimal treatment conditions and also to compare the polymer surface modification induced by plasma jet with the one obtained by another atmospheric pressure plasma source – the dielectric barrier discharge (DBD). The samples were exposed to the plasma jet effluent using a scanning procedure, which allowed achieving a uniform surface modification. The wettability assessments of all polymers reveal that the treatment leads to reduction of more than 40° in the water contact angle (WCA). Changes in surface composition and chemical bonding were analyzed by x-ray photoelectron spectroscopy (XPS) and Fourier-Transformed Infrared spectroscopy (FTIR) that both detected incorporation of oxygen-related functional groups. Surface morphology of polymer samples was investigated by Atomic Force Microscopy (AFM) and an increase of polymer roughness after the APPJ treatment was found. The plasma-treated polymers exhibited hydrophobic recovery expressed in reduction of the O-content of the surface upon rinsing with water. This process was caused by the dissolution of low molecular weight oxidized materials (LMWOMs) formed on the surface as a result of the plasma exposure.

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## 1. Introduction

Non-equilibrium atmospheric pressure plasmas [1–4] have attracted considerable attention because they require low capital cost, can be easily implemented in a continuous production line and also due to their ability to generate highly reactive chemical species at ambient gas temperature [5]. Plasma jets, or plasma plumes are a kind of atmospheric pressure gas discharges where the plasma (usually obtained from a noble gas) is extended beyond the plasma generation region into the surrounding ambience [4,6,7]. The plasma plume length can extend up to several centimeters and can be adjusted by an electric field, a gas flow or a pressure gradient [8,9]. The interaction between the plasma plume and the surrounding atmosphere gives rise to different reactive species that may not be present in the discharge region [10,11]. The gas temperature of plasma jets was estimated by various diagnostic methods [12,13] showing that if jet operation conditions were properly

chosen the gas temperature at the tip of the plasma plume could be quite low (around room temperature). The plasma jets are particularly useful for material treatment, since the gas flow from the jet guides the reactive species close to the surface where they cause surface etching and functionalization [14,15]. Another advantage of the atmospheric pressure plasma jets (APPJs) is that they are not confined by physical walls, thereby making the treatment of irregular-shaped 3D objects possible [16]. However, one limiting factor is the size of the treatment area, which in most APPJ treatments is around 1 cm<sup>2</sup> [17]. To overcome this shortcoming arrays of many individual plasma jets have been developed [18,19]. Another manner for achieving a uniform surface modification is the manipulation of the jet and/or the sample [20,21]. On the other hand, a localized treatment extended over a limited area is desirable for applications in medicine, where for example, only cancer cells have to be targeted without destroying the surrounding healthy tissue. Also, plasma jets in the micrometer scale can be a very useful tool for surface engineering in different fields such as light emission in display panels, lithography, micro and nanotechnology [22–24].

However, still there exist great challenges in understanding the plasma jet physics and chemistry that impede the widespread application of APPJs as a surface modification tool. First of all, jet

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dynamic is not quite understood yet because besides the electromagnetic interaction it also involves the gas flow dynamics, thermal instabilities etc. Also, many different plasma jet configurations with power sources operating over a very large frequency range (1 kHz–50 MHz) are reported in the literature [25–29]. The most common characteristics of plasma jets are summarized in a recent review paper [4].

Operating the jet in ambient air implies collisions, recombination and plasma chemical reactions with the surrounding atmosphere. Therefore, the distribution of the active species in the discharge region, in the effluent, and close to the target may be significantly different [30–32]. For applying the APPJ as a material-processing tool, it is essential to understand the interaction between the active species in the jet downstream point with the surface and determine the size of the modified region as a function of jet parameters [33]. In this work we investigate the surface modification of different polymers by an Ar plasma jet at different operation conditions to find out the optimal process parameters. Comparison between the polymer surface modifications induced by a plasma jet and a DBD treatment has been conducted and the conclusion is that the APPJ is an efficient tool for surface modification. Of course, for obtaining good results the treatment parameters and the plasma jet operation conditions have to be optimized.

## 2. Experimental setup and diagnostics methods

### 2.1. Materials

Prior the routine surface modification of polymers a preliminary plasma jet treatment was conducted. It was aimed to evaluate the size and the location of the plasma-modified spot on the polymer surface as a function of plasma jet parameters and process conditions. This investigation required a large number of samples that had to be cheap and easy to handle. For this purpose we selected a commercial PET (0.3-mm-thickness) cut from colorless plastic bottles. The results from this initial study were used to establish a procedure for the following APPJ treatments that can provide a uniform surface modification over a selected area. To evaluate the surface chemical modification, induced by the APPJ treatment, two typical engineering polymers – polyethylene (PE) and polypropylene (PP), with a simple structure and a high chemical purity, were used. They were provided in the form of 0.1-mm-thick films by Goodfellow, Brazil. Before the plasma processing, the polymeric material were cut into pieces with  $20 \times 15 \text{ mm}^2$  size. All samples were ultrasonically cleaned twice, first in distilled water and after that in isopropyl alcohol for removing surface contaminants. Finally, the samples were dried for 2 h in ambient atmosphere. Upon the plasma treatment some polymer samples were rinsed for 1 min in distilled water, dried for 1 h in ambient atmosphere and after that subjected to further analysis.

### 2.2. Plasma jet

The APPJ used in this work is basically a one-electrode device, which consists of a standard glass syringe (10 ml), whose inner diameter is 15 mm with a nozzle inner diameter of 1.0 mm. An insulating cap, through which the working gas can be admitted to the system, closes the syringe end. Argon was introduced into the syringe at controllable flow rate between 0.2 and 2.5 l/min. A 0.65-mm-thick Ni–Cr wire is installed on the syringe axis and served as a high voltage electrode. The distance between the tip of the wire electrode and the nozzle entrance was about 2 mm. The device was installed vertically using a dielectric support. A metallic platform ( $13.0 \times 13.0 \text{ cm}^2$ ), equipped with a moveable stage that can provide controllable displacements in x–y directions, was

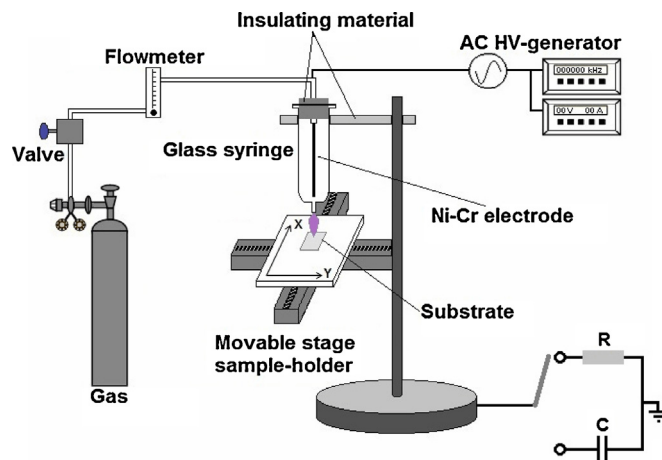


Fig. 1. Schematic diagram of the experimental setup.

situated under the syringe nozzle and acted as a ground electrode. To avoid accidental arcing the whole platform was covered with a 3-mm-thick glass layer (Fig. 1). A Minipuls 4 high voltage power supply (GBS Elektronik GmbH, Dresden, Germany) generates high AC voltages (up to 24 kV peak-to-peak) within the frequency range of 20–40 kHz. A high voltage divider and a serial resistor of  $10 \Omega$  were used for monitoring the applied voltage and the discharge current. The voltage drop across a serial capacitor of 10 nF is proportional to the transferred charge. The signals were displayed on a digital oscilloscope (Tektronix TDS 2024B, 200 MHz).

### 2.3. Polymer treatments

The samples to be treated had rectangular shape (dimensions of  $2.0 \times 1.5 \text{ cm}$ ) and were placed on the glass that covered the grounded platform. Before starting the plasma treatment each sample was aligned central and perpendicular to the syringe axis at a selected distance from the nozzle exit. Argon gas was admitted into the syringe with a controlled flow rate and consequently the plasma jet was ignited and directed onto the sample. Depending on applied voltage and gas flow rate, the length of the Ar plasma plume can extend up to 2.5 cm. As far as the Ar flow remains in laminar regime ( $Re < 2300$ ) the plasma plume length scales with the gas flow rate. However for turbulent gas flow the plasma column easily mixture with the ambient air and as a result the jet became unstable and its length is reduced [33]. For our experimental conditions (Ar gas and syringed orifice diameter of 1.0 mm) the transition between laminar and turbulent regime happens at gas flow around 1.5 l/min and above this value the Ar jet length was actually reduced. Therefore to ensure the maximal extension of the plasma plume ( $\sim 2.5 \text{ cm}$ ) for all material processing we used gas flow rate of 1.3 l/min.

Two series of experiments were conducted to evaluate the degree of polymer surface modification induced by the plasma jet. First, at a fixed jet length (maintained 2.5 cm for all experiments), the sample was static and the distance to the syringe nozzle was varied from 2.0 to 3.5 cm. During the second series of treatments the sample–nozzle distance and the jet extension were kept constant while by using the movable stage the samples were displaced perpendicularly under the plasma jet with a constant velocity of about 6 mm/s. The scanning route consisted of 4 consecutive parallel paths (along the sample's larger dimension) spaced at 3 mm distance. Using these scanning parameters an area of approximately  $200 \text{ mm}^2$  ( $17 \text{ mm} \times 12 \text{ mm}$ ) can be covered for about 15 s. This series of treatments was aimed to achieve a uniform surface modification over the internal part of the sample.

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