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Surface modification of PTFE using an atmospheric pressure plasma jet in argon and argon + CO_2

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ABSTRACT

Polytetrafluoroethylene (PTFE) has many successful engineering applications due to its great chemical stability. However, for some industrial applications, the poor adhesion of PTFE to other materials is a disadvantage. To extend the PTFE application range, several methods have been developed to modify its surface properties. Among these different techniques, plasma surface modification is the most promising one and therefore, an atmospheric pressure plasma jet (APPJ) will be used in this work to modify PTFE samples. Two different discharge gasses have been used: pure argon and an argon/CO_2 mixture and both plasma jets have been examined with optical emission spectroscopy to identify the plasma species present in the discharge. From these results, it was found that the discharge in argon contains argon atoms, nitrogen molecules and metastables, atomic oxygen and OH radicals, while the argon/CO_2 discharge contains also radicals containing CO groups. In a second part of the work, the chemical and physical changes induced by both discharges on PTFE surfaces have been investigated using contact angle measurements, SEM, AFM and XPS. From these results, it was found that exposure times below 20 s lead to a small contact angle decrease due to the introduction of a small amount of oxygen. In contrast, at higher treatment times, the contact angle starts to increase again due to advanced chain scissions leading to a high amount of oligomeric segments on the PTFE surface. As a result of these surface degradation processes, the wettability of PTFE could not be greatly enhanced, however, in the near future, it will be investigated whether these degradation reactions can be eliminated.

1. Introduction

Polytetrafluoroethylene (PTFE) has several excellent properties, such as a high stability against heat and chemical reagents, a high electrical resistance, a low frictional coefficient and a low dielectric constant [1–3]. These properties have led to many successful applications: PTFE can be used as container for reactive and corrosive chemicals, is suitable as insulator in cables and connector assemblies and can be employed as substrate for printed circuit boards [3,4]. Nevertheless, the same lack of reactivity presents a major problem in creating polymer–polymer composites since the inert and hydrophobic surface prevents the establishment of a good interfacial bonding [3–7]. To extend the PTFE application range, several methods have been developed aiming to modify its surface properties. PTFE surface treatments by chemical reduction with sodium naphthalene [8–10], ion beam bombardment [11–13] and plasma modification [14–16] have been reported and all of these treatments were found to lead to improvements in adhesion and wettability. Among the different modification techniques, non-thermal plasma treatment is the most promising one, since it can offer a controllable means of chemically modifying PTFE surfaces without affecting bulk properties [17–20]. Apart from being surface-sensitive, plasma treatments are environmentally benign, easy to control, can be run at room temperature (which is of interest for polymer surfaces) and have a low energy cost [21,22]. However, some drawbacks should be noted, namely aging of the polymer after plasma treatment and the complexity of processes involved during plasma treatment [21,23].

The effects of NH_3 [7,24,25] and N_2 [4,17] plasmas on PTFE have been widely studied and it was shown that these treatments lead to a partial loss of fluorine and incorporation of oxygen- and/or nitrogen-containing groups. In contrast, the effect of oxygen-containing plasmas on PTFE is less clear: for example, Vesel et al. [4] found that an oxygen plasma does not cause any noticeable changes to the PTFE surface, while Chen et al. [26] detected an increase in oxygen amount on the surface coupled with defluorination. Morra et al. [27] observed similar findings, but, in addition, detected significant morphological changes. To elucidate the effect of oxygen-containing plasmas on PTFE surfaces, the present paper will study both chemical and physical changes induced by these plasmas on PTFE. Moreover, in contrast to most of the published literature, plasma modifications will be performed using an atmospheric pressure plasma source, which offers attractive perspectives in today's industrial processes due to

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elimination of vacuum equipment and possibility of in-line processing [28,29]. Among different atmospheric pressure plasma sources, a plasma jet was selected since this discharge can selectively treat specific parts of a substrate and can be easily integrated into existing production lines [30,31]. Moreover, in contrast to most corona and dielectric barrier discharges, atmospheric pressure plasma jets (APPJs) are not limited to flat, thin substrates, but can also be used to modify large three-dimensional structures [30]. Two types of working gasses will be used in this work to modify the surface properties of PTFE: pure argon and argon with a small admixture of CO_2. It should however be noticed that even the pure argon plasma will contain a small amount of oxygen and nitrogen species, since the APPJ used in this study generates a plasma plume that expands into the surrounding air. After describing the experimental procedures, the optical characteristics of the plasma jet will be discussed for both working gasses. In a subsequent section, plasma jet surface treatments of PTFE will be performed and their influence on the PTFE chemical and physical properties will be examined using contact angle measurements (for wettability determination), X-ray photoelectron spectroscopy (XPS, for chemical composition determination), scanning electron microscopy (SEM, for morphology determination) and atomic force microscopy (AFM, for morphology determination).

2. Experimental procedures

2.1. PTFE samples

Commercially available PTFE sheets (Goodfellow, UK) with a thickness of 1 mm are used in the present study and cut into 1.0 cm × 1.0 cm square-shaped samples. Before plasma treatment, the samples are washed in methanol followed by a cleaning step in pure isooctane to remove any surface contamination. Afterwards, the samples are allowed to dry at room temperature before exposing them to the plasma jet.

2.2. APPJ set-up and characterization

A schematic representation of the atmospheric pressure plasma jet is shown in Fig. 1, together with an image of the plasma jet in pure argon. The dielectric barrier discharge (DBD) plasma jet is generated inside a quartz capillary with inside and outside diameters of 6 and 8 mm respectively. The high-voltage electrode, placed inside the capillary, is a stainless steel rod (diameter = 3 mm) with a half-sphere-shaped tip, while the grounded electrode is a stainless steel ring with a length of 10 mm. This grounded electrode is placed around the quartz capillary at a distance of 4 mm from the tip of the high-voltage electrode and 2 mm away from the edge of the capillary. The complete electrode system is surrounded by a Teflon housing and a ceramic ring (thickness: 3 mm) is placed underneath the grounded electrode to prevent spark formation between the electrodes. The plasma jet is generated by applying a sinusoidal wave voltage (fixed frequency of 71 kHz) to the high-voltage electrode with a peak-to-peak value of approximately 6 kV. At an applied voltage of less than 5 kV (peak-to-peak), only a weak radiation zone is observed inside the tube on the tip of the high-voltage electrode. However, an increase in the applied voltage results in the formation of a bright plasma in the inter-electrode gap with a long outflowing plasma propagating in the surrounding air, as shown in Fig. 1. In a first set of experiments, high purity argon (Air Liquide – Alphagaz 2 – purity>99.9995%) is used as discharge gas at a constant flow rate of 3.0 slm (standard liters per minute). Next to pure argon, plasma modifications will also be performed in an argon/CO_2 mixture, which is obtained by adding 0.1 slm CO_2 (Air Liquide – Alphagaz 2 – purity>99.999%) to 2.9 slm argon, keeping the total gas flow rate constant at 3.0 slm. During plasma treatment, PTFE samples are placed on a rotating sample holder (3 mm away from the edge of the capillary) which enables a homogeneous treatment of the polymer surface as confirmed by spatially resolved contact angle measurements.

The voltage applied to the high-voltage electrode is measured using a high voltage probe (Tektronix P6015A), whereas a current transformer (Ion Physics CM-100L) is used to measure the discharge current. The voltage–current waveforms are then recorded with a Tektronix TDS 1002 digital oscilloscope. Using these voltage–current waveforms, the average power W of the discharge is calculated according to the following equation (T = period of the discharge) [32]:

$$W = \frac{1}{T}\int_{t}^{t+T} I(t)V(t)dt \quad (1)$$

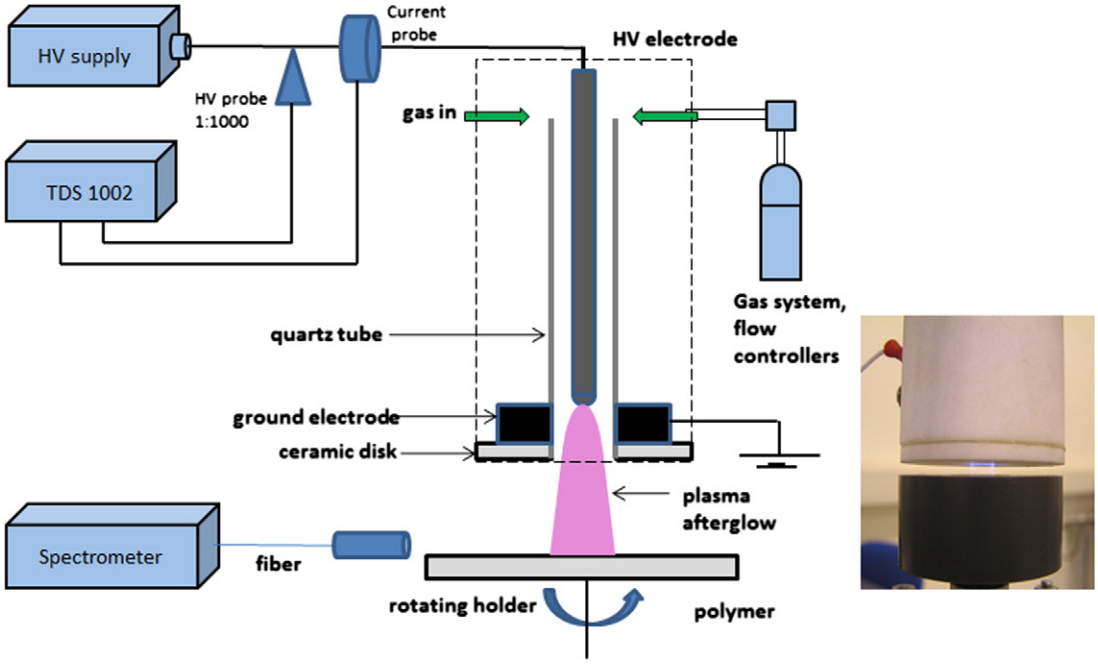

Fig. 1. Experimental set-up of the atmospheric pressure plasma jet with an image of the plasma jet in pure argon.