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Surface modification of polyethylene in an argon atmospheric pressure plasma jet

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ABSTRACT

The surface properties of polyethylene can successfully be altered using argon plasmas. In this work, the surface modification of low density polyethylene (LDPE) using an argon atmospheric pressure plasma jet (APPJ) is profoundly investigated. The surface modification is examined using different analysing techniques namely, water contact angle (WCA) measurements for the wettability and X-ray photoelectron spectroscopy (XPS) for the chemical composition. Particular attention is paid to the treatment distance between the plasma jet capillary and the LDPE foil and the applied treatment time. At treatment distances between 5 and 15 mm, the WCA can be reduced with more than 70% within a treatment time of a few ms. XPS measurements reveal that this is due to the incorporation of oxygen containing groups and especially the increased implementation of the O–C═O group has a big influence. At treatment distances above 15 mm, the wettability decreases with increasing treatment distance. The wettability can however be enhanced by increasing the treatment time. Ageing considerations show that the loss in treatment efficiency is restricted to only 25%, meaning that even after 14 days of ageing the WCA reduction upon plasma treatment is still more than 40%. Based on the above mentioned results, the most appropriate parameters can thus be selected to provide an efficient plasma treatment of LDPE using the argon APPJ.

1. Introduction

Polyethylene (LDPE) is one of the most widespread polymers used for industrial and medical applications due to its excellent material properties (low density, high flexibility and high chemical resistance) [1]. However, despite these excellent characteristics, LDPE is often unsuitable for use due to its low surface free energy, leading to poor wettability and poor adhesion [2]. In the past, improvements in wettability and adhesion have been obtained using wet chemical processes; however, ecological requirements force the industry to search for alternative environmentally friendly methods. Recently, plasma treatment of polymers has been gaining popularity as a surface modification technique since it does not require the use of water and chemicals. Therefore, it can be considered as an environmentally benign technology. Moreover, it is a versatile technique that only affects the first few atomic layers at the surface without affecting the bulk properties [3,4]. Plasmas can induce topographical modifications, [5] change the chemical composition [3] of a surface and can also be used for cleaning and deposition purposes. In the preceding works the method has already shown its effectiveness, using different types of non-thermal plasmas operating at low, medium or atmospheric pressure [6–10].

As in all research fields, also in the plasma technology research area, there is a constant evolution of the used techniques. Today, low pressure and atmospheric pressure plasmas have found widespread use for the pre-treatment of polymers in industrial applications. In particular, atmospheric pressure plasma jets (APPJ) have gained a lot of interest in the last few years, because they are easy to integrate into existing production lines and can selectively treat specific parts of a substrate. Also, in contrast to most corona treatments (and dielectric barrier discharges), APPJs are not limited to flat and thin substrates but can also be used for large three-dimensional structures.

Over the last few years, a whole range of papers has been published regarding the effective application of plasma jets for the modification of polymer materials [11–13]. However, a detailed study of the influence of different plasma treatment parameters on LDPE using the plasma jet working at atmospheric pressure in argon has not yet been presented. Therefore, in this work, the influence of plasma jet parameters such as plasma treatment time and treatment distance between the ground electrode and the foil on the surface modification of LDPE will be explored in detail. The effects will be studied for different applied powers at a fixed argon flow rate of 1.25 slm (standard litres per minute). At this

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flow rate, turbulence will be avoided in the argon flow and the provided afterglow of the plasma is maximal [14]. Finally, the ageing effect of the plasma treated LDPE films will be investigated in detail.

2. Materials and methods

2.1. Polyethylene

The used polyethylene foil is a low density polyethylene (LDPE) film with a thickness of 0.1 mm. This commercially available LDPE foil was purchased from Goodfellow Cambridge Ltd. and has not been subjected to any pre-treatment step prior to plasma modification.

2.2. Atmospheric Pressure Plasma Jet (APPJ)

An atmospheric pressure plasma discharge is generated inside a quartz capillary with an inside and outside diameter of 1.3 and 3.0 mm respectively. Fig. 1 shows the used experimental set-up along with an image of the argon APPJ. The high-voltage electrode is a tungsten wire (diameter 1 mm) with a half-sphere-shaped tip and is placed inside the quartz capillary. The ring-shaped ground electrode (length = 10 mm) is placed around the capillary at a distance of 40 mm from the high-voltage electrode and 20 mm away from the edge of the capillary. High purity argon (Air Liquide — Alphagaz 1) is used for the plasma generation with a flow rate of 1.25 slm. At this flow rate, turbulence is avoided in the argon flow, as turbulence occurs from 1.5 slm on, and the length of the afterglow is maximal [14]. LDPE samples are modified with the plasma jet by scanning the polymer surface with adjustable scanning velocities (0.08–4.5 m min^{-1}). The jet is generated by applying an AC voltage (fixed frequency = 60 kHz) to the high-voltage electrode with peak-to-peak values ranging from 7 kV to 14 kV. The voltage applied to the high-voltage electrode is measured using a high voltage probe (Tektronix P6015A), whereas the discharge current is monitored by measuring the voltage over a 50 Ω resistor, which is connected in series between the ring electrode and the ground. The voltage–current waveforms are then recorded using a Tektronix TDS 1002 digital oscilloscope. Using these voltage–current waveforms, the average power P of the discharge is calculated according to the following equation (T = period of the discharge) [15]:

$$P = \frac{1}{T}\int_{t}^{t+T} I(t)V(t)dt. \tag{1}$$

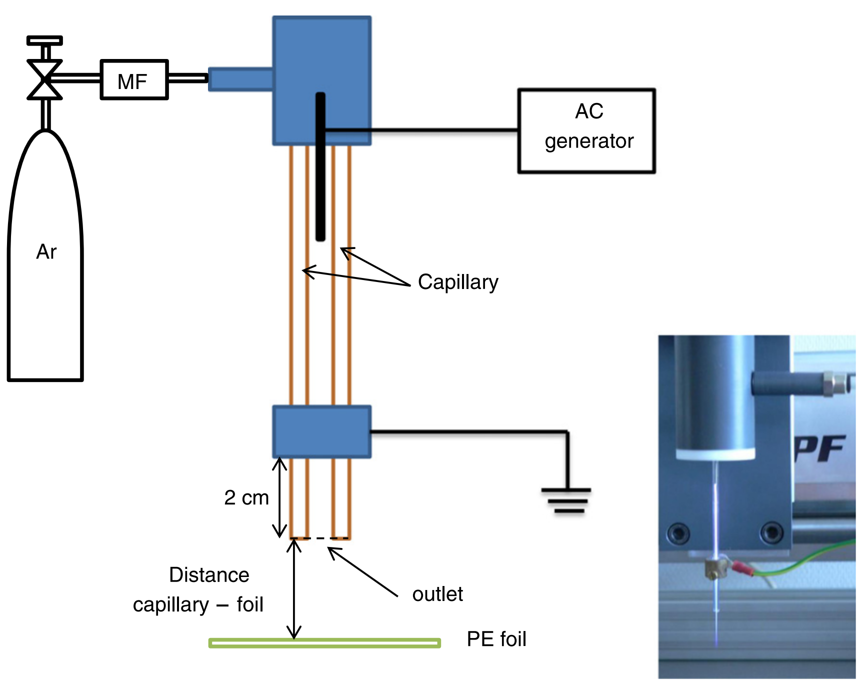
During the LDPE surface modification experiments, the applied plasma power has been varied between 3 and 11 W. To enable an objective comparison between the plasma treatments conducted at different discharge powers, the results will be presented as a function of energy density (J cm^{-2}). This value is calculated by multiplying the plasma exposure time with the plasma power and by dividing this value by the cross section of the capillary. The plasma treatment time t can be obtained by dividing the active diameter of the jet (=1.3 mm) to the plasma scanning velocity.

2.3. Water Contact Angle measurements (WCA)

The wettability of the untreated and plasma treated LDPE films is evaluated using static water contact angle measurements. The static WCA values are obtained at room temperature using a Krüss Easy Drop system. Within minutes after plasma treatment, a 2 μl drop of distilled water is deposited on each sample. Droplets are placed at different positions and images are captured a few seconds after deposition of each drop. Based on the imaged water drop profile, the static WCA value is obtained using Laplace–Young curve fitting. Every reported WCA value in this work is the average of 10 droplets placed at different positions on one single sample.

2.4. X-ray Photoelectron Spectroscopy (XPS)

Besides contact angle measurements, the chemical composition of the LDPE samples is obtained by XPS. XPS measurements are performed on a PHI VersaProbe II spectrometer employing a monochromatic Al K_α X-ray source ($h\nu$ = 1486.6 eV). Survey scans and high resolution C1s peaks are recorded at a take-off angle of 45° relative to the sample surface. The XPS survey scans are processed using MultiPak software and



(a) (b)

Fig. 1. Experimental set-up (a) and visual view (b) of the plasma jet.