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Surface modification of polymer films using an atmospheric-pressure plasma jet

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Abstract: An atmospheric-pressure plasma jet (APPJ) is used to increase the wettability of polypropylene (PP) polymer films. Reduction in contact angle from 95 to 50 degrees was measured for treatment times of 1 - 10 seconds. Contact angle reductions of PP as a function of distance between APPJ and PP surface, and oxygen gas admixture, suggest that the surface reaction mechanism is related to the atomic oxygen density produced in the APPJ.

Keywords: atmospheric-pressure plasma jets, polymer films, surface modification

1. Introduction

Polymers such as polypropylene (PP) are used in many applications, from food containers to surgical implants, and packaging to textiles [1]. The applications for these polymers rely on the fact that they are a thermoplastic with a good resistance to heat, chemicals, and fatigue. It is also semi-rigid and translucent. One of the few downsides to these polymers, for manufacturers who want to adhere inks or glues to its surface, is that it is has low wettability. Nowadays, non-thermal plasmas are commonly used to improve the surface properties of these polymers to allow better adhesion and printing [2]. Since these plasmas only treat the surface of the polymer film, the integrity and properties of the bulk material are not compromised.

A wide variety of plasma systems, both at traditional low-pressure and at atmospheric pressure, have been used to treat PP films to improve their surface properties, e.g., [3-6]. Despite the fact that many of these plasmas operate under very different conditions, i.e., operating gases, voltage waveforms and frequencies, and geometries, they all are capable of improving the adhesion properties of PP surfaces. It is believed that the poor adhesive properties of untreated polymer films are due to a lack of polar groups on the surface [7]. The plasma can change this by either adding polar groups to the surface, or breaking surface bonds, creating polar end groups. Although this general concept is fairly well established, the details of the chemical processes involved both at the surface as well as inside the plasma are not fully understood. In other words, by what mechanisms is the polymer film surface modified and how can the plasma design be optimised to achieve maximum modification in the least amount of time? This paper we will make a link between direct measurements of plasma radical densities and changes in polymer surface properties for a variety of operating conditions of an atmospheric-pressure plasma jet. The overall aim of this research is to investigate the underpinning plasma chemistry that is at play in surface modification of PP films in order to optimise the plasma design and operating conditions for industrial applications.

2. Experimental arrangement

The atmospheric-pressure plasma jet (APPJ) that was used is schematically shown in Fig. 1.

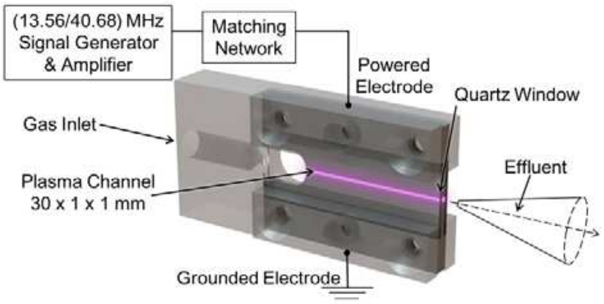

Fig. 1. Schematic diagram of the Atmospheric-Pressure Plasma Jet used in this work.

It is a well-characterised device in terms of its plasma composition and chemistry, e.g., [8-10]. It consists of two parallel, stainless steel electrodes, sandwiched between 2 quartz glass plates, creating a plasma channel of 1 x 1 x 30 mm. Helium gas with admixtures of up to 1% oxygen flow through this channel at 1 standard litre per minute (slm). One of the electrodes is driven, via a matching network, with a radio-frequency voltage of 13.56 MHz, creating a plasma inside the plasma channel. This plasma flows out of the device, into open air, creating a neutral, radical-rich effluent that is made to interact with polymer films. The APPJ is facing vertically downwards towards a polymer sample surface. The distance between the APPJ nozzle and the sample was varied between 3 and 50 mm.

The change in the surface properties of the treated PP films was monitored by measuring the change in wettability using a contact angle analyser (Dyne Technology, Theta Lite). It consists of a camera that looks across the polymer surface, and a syringe with a needle tip to drop droplets of water onto the surface. Images from the camera are used to measure the contact angle between the water droplet and the polymer surface.

The polymer films used in this work were PP with a thickness of 100 µm (Goodfellow Cambridge Ltd).

3. Results

Important parameters for industrial applications of these treatments are the maximum amount of change in wettability that can be achieved and the duration of the treatment that is needed to achieve the desired change. To investigate the required treatment time, we exposed samples of PP film to a range of durations of plasma treatment with the APPJ. The APPJ was operated with 1 slm of He gas with an admixture of 0.5% O_2, and 35 W of RF power from the generator. The distance between the APPJ nozzle and the PP surface was 3 mm. The measured contact angles after the various treatment durations are shown in Fig. 2.

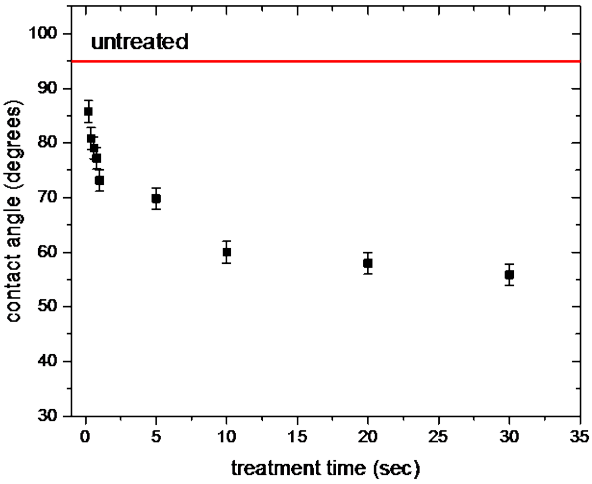

Fig. 2. Measured contact angle of PP film as a function of treatment time with the APPJ. The solid line indicates the contact angle for untreated PP samples.

A significant change in the PP wettability can already be seen for short APPJ treatment times, e.g., a 1-sec treatment reduces the contact angle from 95 to 73 degrees. For many industrial applications speed is important and a 20 degree reduction in contact angle is often sufficient. Nevertheless, it takes roughly 10-sec treatments to reach the full effect of APPJ treatment; a reduced contact angle of about 55°. Longer treatment times do not decrease the contact angle further. The observed relation with treatment time suggests that the surface reactions reach saturation after a certain time, i.e., after about 20 sec. All the sites on the surface available for modification by the plasma have undergone change and no further reduction in wettability can be achieved.

To further investigate the plasma chemistry at play, the treatment distance, i.e., the distance between the APPJ nozzle and the polymer surface was varied between 3 and 50 mm. For each distance, several PP samples were treated for times ranging from 5 to 60 seconds. The results of these experiments are shown in Fig. 3. A similar saturation behaviour as was observed in Fig. 2, is again seen for all treatment distances. That is, after about 50 - 60 seconds the maximum change in contact angle has been reached. Interestingly, the value of the saturated contact angle scales with treatment distance; that is, for 3 mm the contact angle goes down to 50° while at a distance of 50 mm, it does not go below 83°.

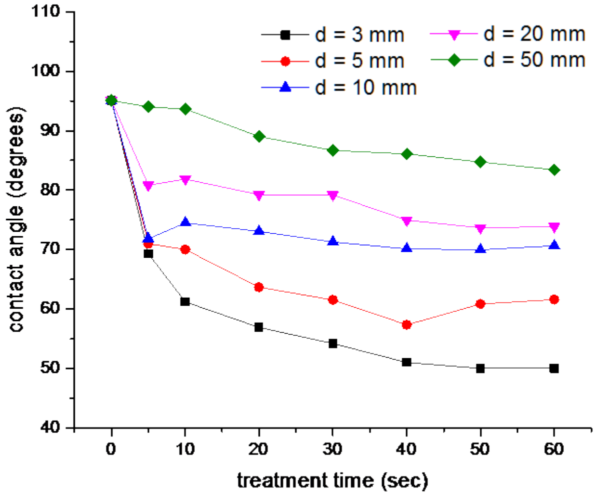

Fig. 3. Measured contact angle as a function of treatment time for different distances between the APPJ and the polymer surface. The points at t=0 sec represent the contact angle for untreated PP.

Finally, the oxygen admixture to the helium feed gas was varied. An APPJ treatment time of 60 sec was chosen, which was verified to be enough to reach contact angle saturation for all admixtures. Fig. 4 shows the minimum contact angle as a function of oxygen admixture.

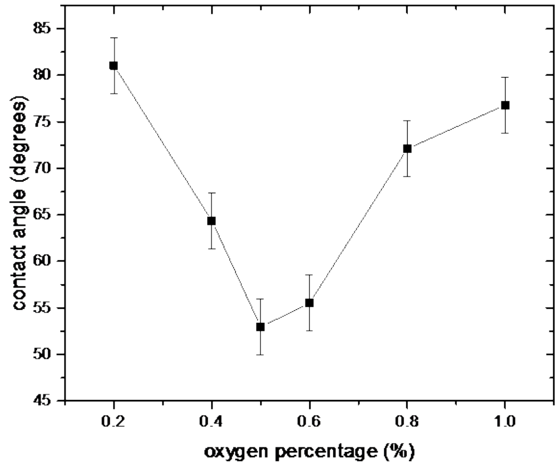

Fig. 4. Measured contact angle as a function of percentage of O_2 admixture to the He feed gas. APPJ treatment was for 60 sec, at a distance of 3 mm from the surface.

It can be seen that there is an optimum effect, i.e., minimum contact angle for 0.5% O_2. Both smaller and larger O_2 admixtures result in contact angle reductions 25 degrees less than what is observed at 0.5%.

4. Discussion and outlook

It is well known that these types of APPJs produce large quantities of several reactive oxygen species, e.g., O, O_3, O_2^*(singlet delta oxygen (SDO)), which have been measured directly for varying operating conditions [11-13]. Knake *et al.* measured 2D maps of the absolute O densities in the effluent of an APPJ and found that the density drops exponentially from the nozzle up to about 50 mm [10]. We observe a reduction in the effect of the plasma treatment of PP with distance between the APPJ and the surface, similar to the measured O densities, suggesting a relation between the two. Furthermore, Knake *et al.* also measured O densities as function of oxygen admixture [10] and found an optimum at 0.5%. Again, this correlates directly to what is observed in Fig. 4, a maximum effect of surface modification at conditions with maximum O production.

In contrast, Sousa *et al.* measured SDO densities for varying oxygen admixtures and found a decreasing trend with increasing admixture [12]. Furthermore, Ellerweg *et al.* measured an increase of ozone with increasing oxygen admixture [13]. Neither of these trends corresponds to what is measured in Fig. 4: suggesting that they are not the primary species responsible for the surface modification of PP. Therefore, we conclude that our experiments indicate that the surface modification of PP is related to atomic oxygen, O, from the APPJ.

Even though exact reaction mechanisms cannot be derived from our experiments, it is possible from Figs. 3 and 4 to gain some general insight into the types of reactions that take place on the surface of the PP sample. If the reactions were limited by the number of surface sites that are available, the total effect would scale with the total flux of O to the surface. In other words, even if the density of O at the surface is lower, applying the treatment for longer would compensate this and the same total flux would result in the same final effect, i.e. all surface sites have been modified. This is not what is observed, if the O density at the surface is smaller, e.g., further away (Fig. 3), the minimum contact angle is not as small as when the APPJ is closer to the sample, even when the treatment time is increased. This suggests that for the reactions at the surface, the density of O is important, not the total flux.

Detailed modelling of both the chemistry inside the plasma and plasma effluent as well as the interactions with the PP surface, in combination with experiments directly measuring relevant species at the polymer surface, are needed to further clarify the exact reaction mechanisms at play. This increased understanding of the process can aid with the design and optimisation of future plasma devices for specific applications.

5. Acknowledgments

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