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Surface treatment of high density polyethylene (HDPE) film by 50 Hz dielectric barrier discharge produced in air and argon/air mixture at atmospheric pressure

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ABSTRACT
Thin films of high density polyethylene (HDPE) are treated for improving hydrophilicity using non-thermal plasma generated by 50 Hz line frequency dielectric barrier discharge produced in air and argon/air mixture at atmospheric pressure. HDPE samples before and after the treatment are studied using contact angle measurements, surface free energy calculations and atomic force microscopy (AFM). Distilled water (H_2O), glycerol ($C_3H_8O_3$) and diiodomethane (CH_2I_2) are used as test liquids. The contact angle measurements between test liquids and HDPE samples are used to determine total surface free energy using sessile drop technique. HDPE films show a remarkable increase in surface free energy after plasma treatment. AFM analysis of the plasma-treated HDPE films shows that plasma treatment introduces greater roughness on the surface leading to the increased surface free energy. Furthermore, it is found that introducing a small quantity of argon can enhance the surface treatment remarkably.
Keywords: Thin films, polymer, atmospheric pressure dielectric barrier discharge, hydrophilicity, sessile drop technique.

I. INTRODUCTION

Polymers are used in a wide variety of applications including packaging and labeling, textiles, stationery, automotives, laboratory equipment, etc. A low surface energy may be desirable in them for several applications, but for other applications it is a disadvantage, which has to overcome [1]. High density polyethylene (HDPE) is one of the most widely used polymers in the industries. As the surface energy of HDPE is also quite low, its surface properties such as hydrophilicity, adhesivity and printablility do not often meet the requirement for industrial applications. In order to extend its application range, different methods have been developed to modify its surface properties [2, 3]. Among them, atmospheric pressure non-thermal plasma treatment is a convenient and environmentally friendly way to obtain these modifications by introducing new chemical groups at the surface without affecting the bulk properties. However, most of such processes are conducted at low-pressure and high frequency, which needs expensive vacuum equipment and only batch treatment is possible, and therefore it is difficult to apply these processes to large-scale objects, especially under the condition of continuous treatment. Recently, much attention has been paid to the use of non-thermal plasmas under atmospheric pressure for surface modification of polymers. Among various atmospheric pressure non-thermal plasma sources, atmospheric pressure dielectric barrier discharge (APDBD) using line frequency (50 Hz) is attractive for industrial applications as it avoids the high costs associated with vacuum-based plasmas and overcomes the power supply heating deficiency of high frequency plasmas. This environmentally friendly dry treatment can modify the surface properties of materials without changing the chemical and physical bulk properties [4]. In the recent past, a great deal of work has been devoted to the DBDs working in the homogeneous glow regime. While it has been demonstrated that homogeneous diffuse discharges can indeed be obtained in barrier discharge configurations, this is possible only when special, quite restrictive conditions are met. Diffuse discharges of this type would have obvious advantages over the more common filamentary ones, especially for the uniform activation of material surfaces on the entire area exposed to the discharge. However, in practice, it is difficult and tricky to reliably control homogeneous glow discharges at atmospheric pressure. The filamentary DBD is an excellent source of microdischarges containing energetic electrons [5].

In this study, HDPE film samples are treated in atmospheric pressure dielectric barrier discharge (APDBD) using line frequency (50 Hz) in air and argon/air mixture. Surface analysis and characterization of the samples are performed using

contact angle measurements, surface free energy calculations and atomic force microscopy (AFM).

II. EXPERIMENTAL SET-UP AND PROCEDURE

For plasma surface treatment of HDPE films, atmospheric pressure dielectric barrier discharge (APDBD) source is used. The general view of the experimental set-up is shown in figure 1. For the discharge, two rectangular copper electrodes with dimensions 5 cm × 3.5 cm × 1 cm are used. The lower electrode is covered by a polycarbonate (PC) plate with dimensions 10 cm × 8 cm × 0.2 cm as a dielectric barrier, separated by a gap between two electrodes, thus resulting in DBD. The upper electrode is fixed and the lower electrode is movable in a vertical scale to adjust the electrode gap.

The discharge is generated via line frequency (50 Hz) high voltage (maximum peak-to-peak value of 50 kV) power supply which is simply a step-up transformer. The upper electrode is connected to the high voltage power supply through a ballast resistor in series to limit the current. The lower electrode is grounded through a shunt resistor across which the discharge current is measured. The voltage applied to the electrodes is measured with a voltage divider which is composed of two resistors of 60 MΩ and 47 kΩ. The characteristic of the discharge is sensitive to the electrode gap, applied voltage and ballast resistor which effect the uniformity of the surface treatment. The electrical characterization of the discharge performed in previous experiment [6] shows that the discharge is uniform with electrode gap 3.5 mm, applied voltage 13 kV and ballast resistor 20 MΩ. Thus, similar electrode gap, applied voltage and ballast resistor are used in the experiment.

Commercially available high density polyethylene (HDPE) films of thickness 0.01 mm and with dimensions 3 cm × 2.5 cm from Goodfellow Ltd., UK are used as samples for plasma treatment. Before the treatment, the samples are washed in propylene and then washed in distilled water, ultrasonicated for ten minutes, and dried at room temperature. The plasma surface treatment is performed by placing the HDPE samples on the dielectric material, i.e., the polycarbonate (PC) plate in between the two electrodes at room temperature. Dry ambient air and a mixture of argon and air are used as a plasma gas. Argon with a flow rate of about two liters per minute is used in case of argon and air mixture. The plasma treatment time is varied in a range from 5 s to 60 s. HDPE samples before and after the treatment are studied using contact angle measurements, surface free energy calculations and atomic force microscopy (AFM). Static contact angle measurements are made before the treatment and immediately after the treatment by dropping 4 μ*l* of distilled water (H_2O), glycerol ($C_3H_8O_3$) and diiodomethane (CH_2I_2) on the surface. Different liquid drops on the HDPE surface are imaged using CCD camera and the contact angles are measured using Rame hart contact angle goniometer, model: 200. The values of the static contact angle are the average of four measured values. The static contact angles between the test liquids and HDPE samples are used to determine total surface free energy using sessile drop technique. The morphology of the HDPE surface before and after the treatment are investigated by using an atomic force microscopy (AFM) (Nanoscope III SPM) in ambient conditions.

III. RESULTS AND DISCUSSION

Surface treatments are performed by setting the electrode gap to 3.5 mm with applied voltage 13 kV and ballast resistor 20 MΩ. The changes in surface properties are studied by varying the treatment time.

Contact angle measurement:

Figure 2 shows the variation of the static water contact angle on the surface of the HDPE film with the APDBD treatment time, both in air and in argon/air mixture. In this case, it is seen that a rapid decrease in the static water contact angle takes place with the treatment time up to 10 seconds which shows that a strong increase of wettability in the HDPE surface is induced by APDBD treatment. The static water contact angle observed is found to change from 92.8° for the untreated (control) sample to the values of 63.7° after 10 seconds of APDBD treatment in air, and 51.4° after 10 seconds of APDBD treatment in argon/air mixture. When the treatment time exceeds 10 seconds, the measured static water contact angle seems to reach nearly a saturation state suggesting that the physical and chemical changes induced by the plasma are also in saturation state when the treatment time (plasma dose) is in excess of a certain critical value. Moreover, it is clearly seen that the APDBD treatment in argon/air mixure decreases the static water contact angle more than the APDBD treatment in air with the same treatment time which clearly proves that a strong increase of wettability in the polymer surface can be induced by the APDBD treatment by introducing a small amount of argon in the discharge gas environment.

Surface free energy measurement:

The contact angles between the test liquids and HDPE surface are measured in order to determine the total surface free energy using sessile drop technique and three liquid model. The surface free energy is calculated from Young-Dupre equation [7, 8] using the contact angle. The variation of surface free energy and its components with treatment time of HDPE in air and argon/air plasma are shown in Figures 3 and 4 respectively. The surface free energy

of untreated HDPE is about 35.0 mJ/m^2. As can be seen from the figure 3, the value of the surface free energy reaches about 43.6 mJ/m^2 after 10 seconds of the treatment in air plasma. Similarly, it can be seen from the figure 4 that the value of the surface free energy reaches about 48.2 mJ/m^2 after 10 seconds of the treatment in argon/air plasma. In both cases, it is found that the further treatment of HDPE after 10 seconds does not lead to any significant changes in the surface free energy and its components. Increased surface free energy leads to increased wettability. Since HDPE is the polymer which does not contain oxygen in the chain, both the polar and dispersive components of surface free energy are considerably increased by the plasma treatment.

AFM analysis:

In order to compare the polymer surface modifications in air plasma and argon/air plasma, the polymer samples are treated in the discharge in air and argon/air mixture with a flow rate of about two liters per minute. As already mentioned above, the treatments are performed with electrode gap 3.5 mm, applied voltage 13 kV rms and ballast resistor 20 MΩ. The AFM imaging is performed with Nanoscope III SPM atomic force microscope to study the surface morphology of HDPE before and after the plasma treatment. The AFM images of untreated and treated polymers in air and argon/air plasma are shown in figures 5 to 10. The morphology of the treated surfaces appear to be quite different than the untreated one. This is the result from the etching effect of the plasma treatment. The main species in the plasma which are responsible for the etching effect are positive ions and photons, with ability of breaking primary chemical bonds and introducing cross-linking [9, 10]. It can be seen that the treatment in argon/air plasma causes relatively higher roughness of the treated surface than the air plasma treated surface.

Figure 5 shows the 2-D AFM image of untreated sample of HDPE and profile of a water droplet on the surface, showing measured contact angle of 92.8°. The morphology of the untreated HDPE appears comparatively smooth. Figure 6 shows the 2-D AFM image of HDPE sample that has been treated in air plasma for 60 seconds and profile of a water droplet on the surface, showing measured contact angle of 54.0°. As can be seen from the figure, the surface of the air plasma treated HDPE is changed with slightly increased roughness of the surface compared to the untreated HDPE. Figure 7 shows the 2-D AFM of HDPE surface treated in argon/air plasma for 60 seconds and profile of a water droplet on the surface, showing measured contact angle of 46.1°. It is now clearly seen that the surface of the argon/air plasma treated HDPE is changed drastically with highly increased roughness of the surface compared to both the untreated HDPE and air plasma treated HDPE. As can be seen, the air plasma has only a slight effect on the morphology of HDPE. These results can also be observed in 3-D AFM images presented in figures 8, 9 and 10.

The surface of the argon/air plasma treated HDPE is found to have much higher roughness of the surface compared to the untreated sample. It is known that the argon plasma does not allow incorporation of new chemical species into the polymer chains. Despite this, argon/air plasma treated surface gets much more oxygen-containing polar groups than the untreated surface. This phenomenon can be attributed to the fact that argon has lower breakdown potential than air [9]. The blending of it can make the discharging more symmetrical which can lead to ampler plasma ionization.

IV. CONCLUSIONS

The set of experimental results on the surface treatment of high density polyethylene (HDPE) film with atmospheric pressure dielectric barrier discharge (APDBD) using line frequency (50 Hz) both in air and argon/air mixture prove that this kind of discharge is a convenient and efficient source of non-thermal plasma and can be successfully used for the surface hydrophilization. This fact is confirmed by the contact angle measurements. It has been shown that high density polyethylene (HDPE) surface can be treated to achieve high hydrophilicity with relatively short treatment time (up to 10 seconds). Longer exposure time do not cause significant changes in static contact angle values which means that saturation of plasma effect occurs. The contact angles are measured over an extended area of the treated sample and show a dispersion lower than 2.5° which is within the limit of experimental error. This implies that the surface treatment is uniform despite the fact that the discharge consists of a series of microdischarges randomly distributed over the electrode surface. The steep diminution of the contact angles on treated samples compared to the untreated one shows the strongly increased wettability induced by APDBD even after such short treatment times. This behaviour can be attributed to strong surface oxidation. The molecular oxygen in the contacting air is activated, ionized and dissociated in the discharge to give extremely reactive oxygen species that react readily with the substrate surface [5].

It is well known that the plasma treatment increases the surface free energy of polymers because of strong surface oxidation in the discharge. Many authors have performed XPS measurements on plasma-modified polymer films, showing the presence of oxygen-containing functionalities on the polymer surfaces after the plasma treatment [11].

The results of AFM show that a slight increase in roughness of the polymer surface takes place when air plasma treatment is applied, and a large increase in roughness of the polymer surface takes place when argon/air plasma treatment is applied showing that a small amount of argon can enhance the surface treatment remarkably. Furthermore, the results of AFM are in good agreement with the static contact angle measurements.

It is believed that microdischarges in APDBD strike randomly; however, it is not always true. Under certain conditions, microdischarges interact with each other and arrange themselves into a regular pattern [12]. The microdischarge pattern affects the performance of APDBD treatment, especially in applications where spatial uniformity is required because it results in superior quality of the treated surface. After the experimental results discussed above, it is better to express one thing that usually uniform plasma treatment is desired but it is necessary to emphasize that uniform plasma treatment requirement does not always necessitate uniform discharge. It is found that microdischarges arrange themselves into regular pattern gradually over time rather than suddenly.

V. ACKNOWLEDGEMENT

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FIGURES

Figure 1

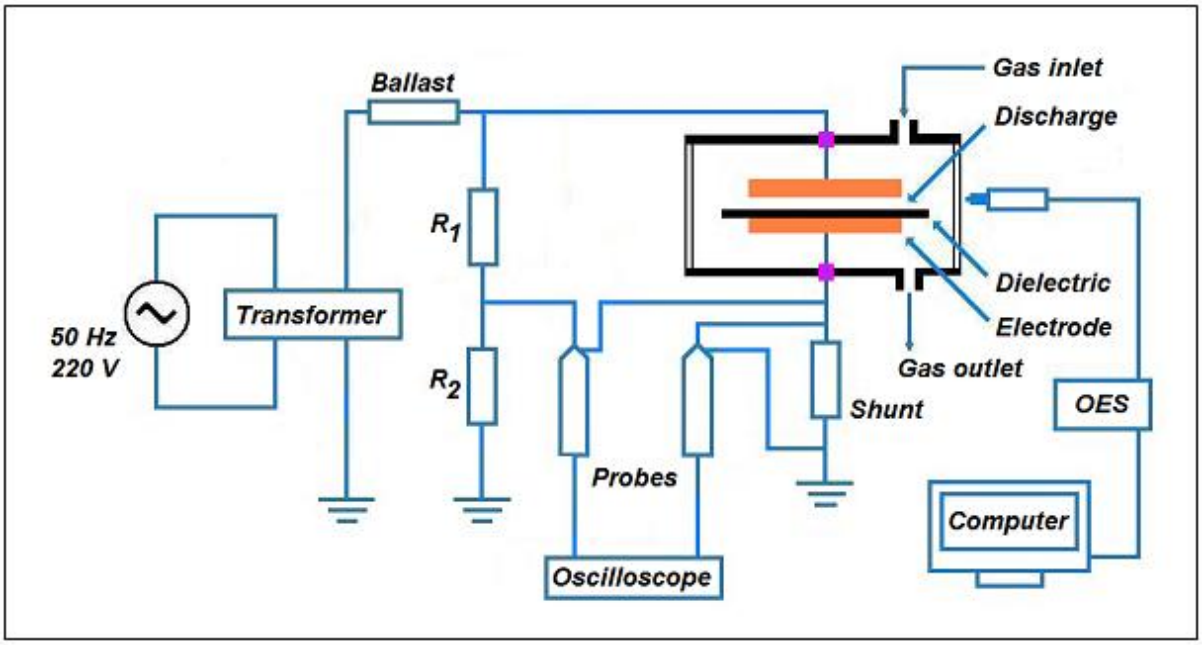

Figure 2

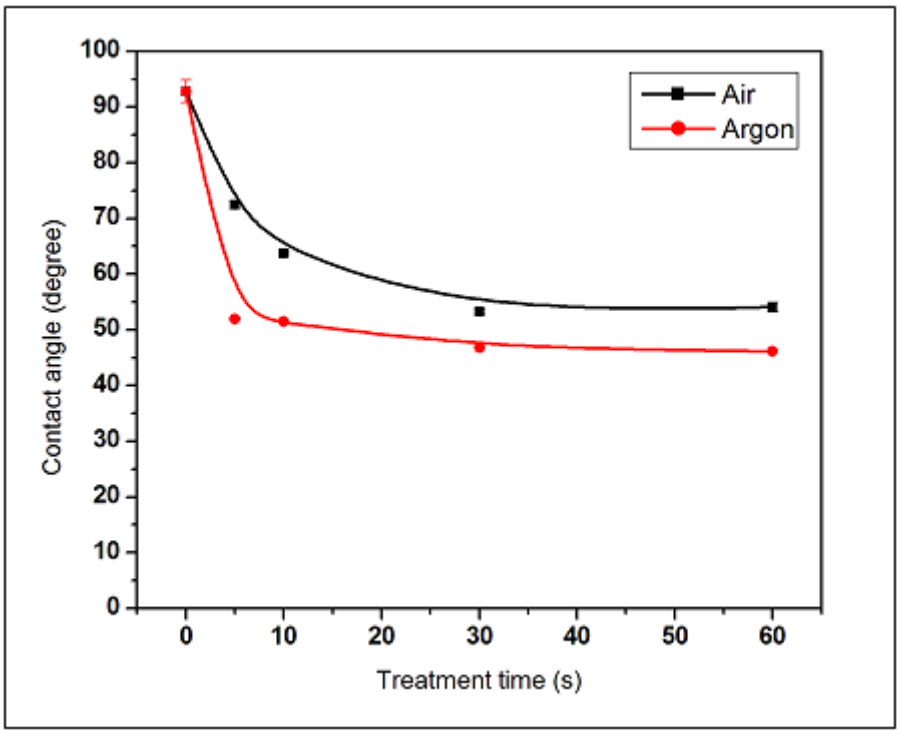

Figure 3

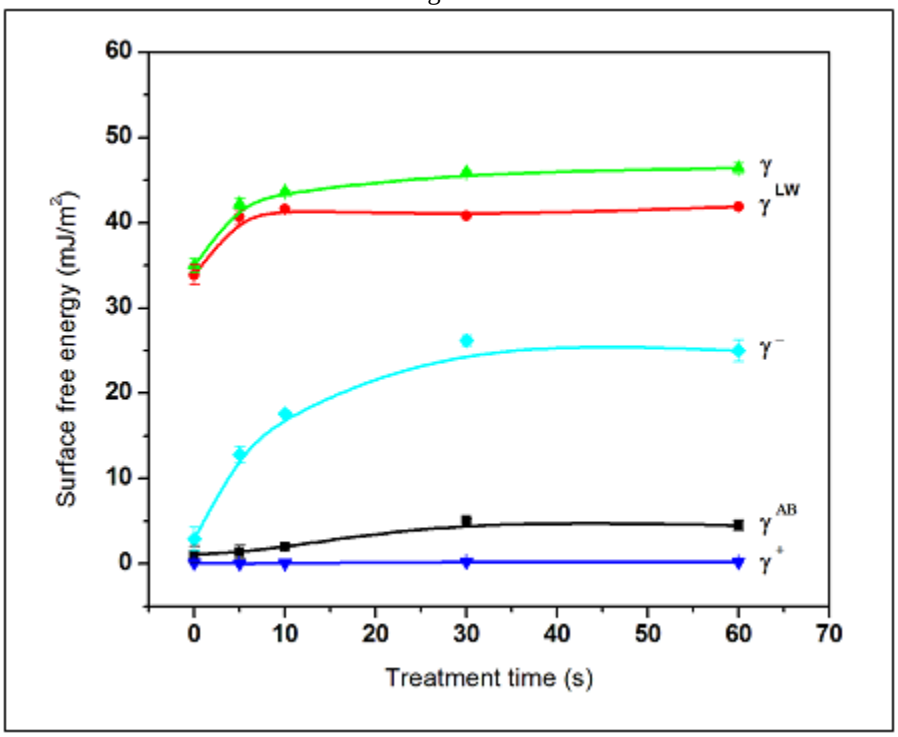

Figure 4

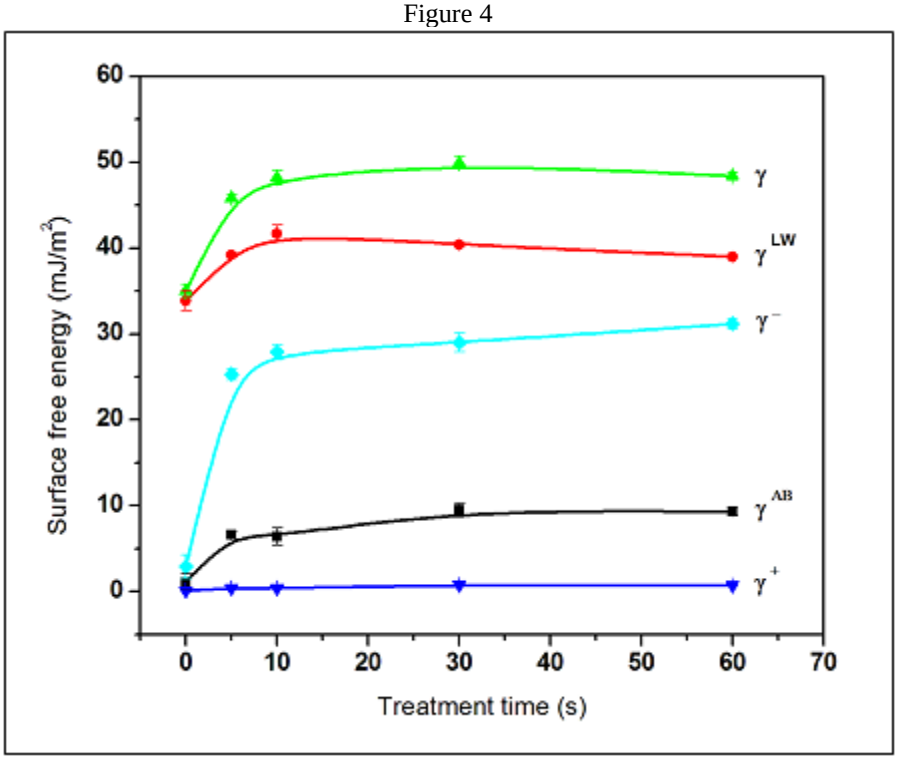

Figure 5

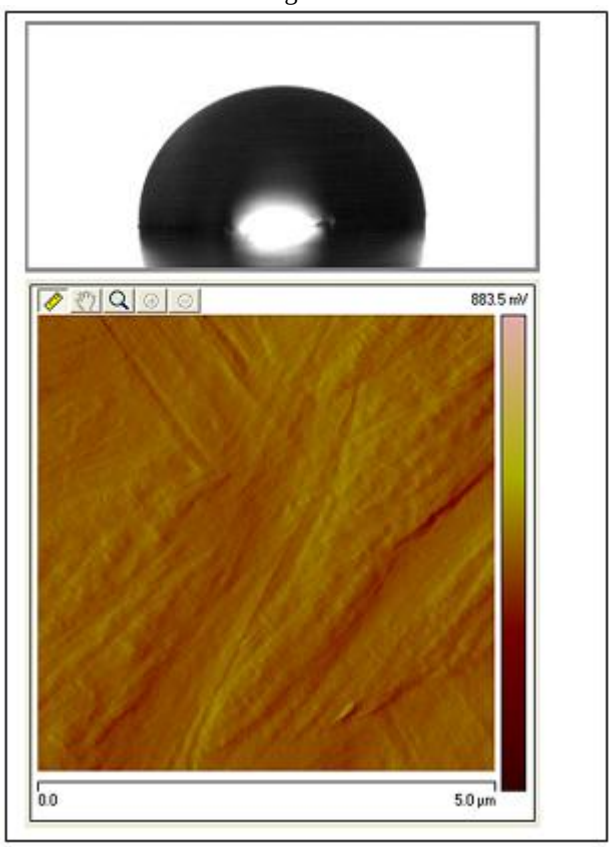

Figure 6

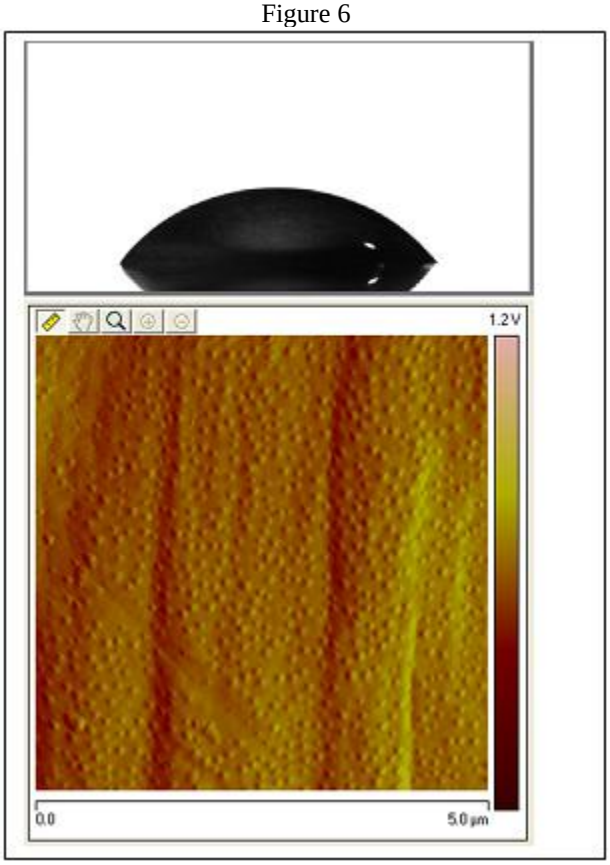

Figure 7

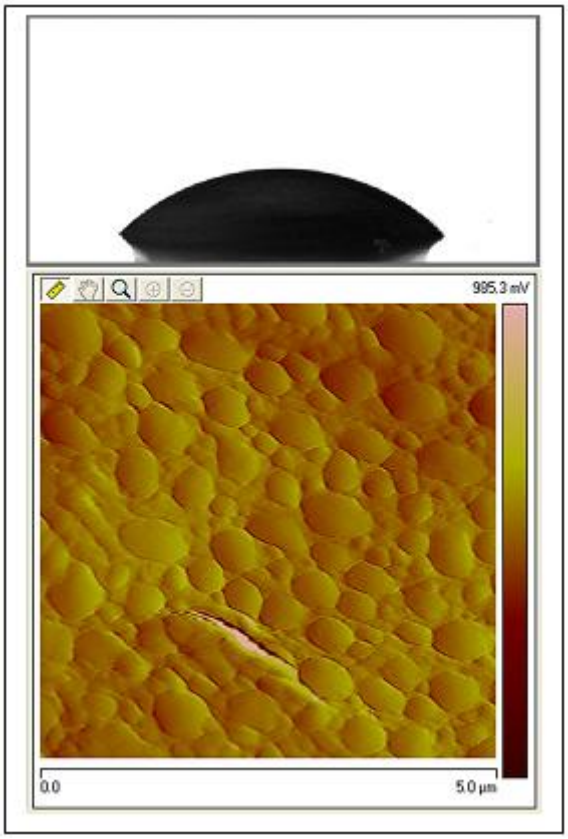

Figure 8

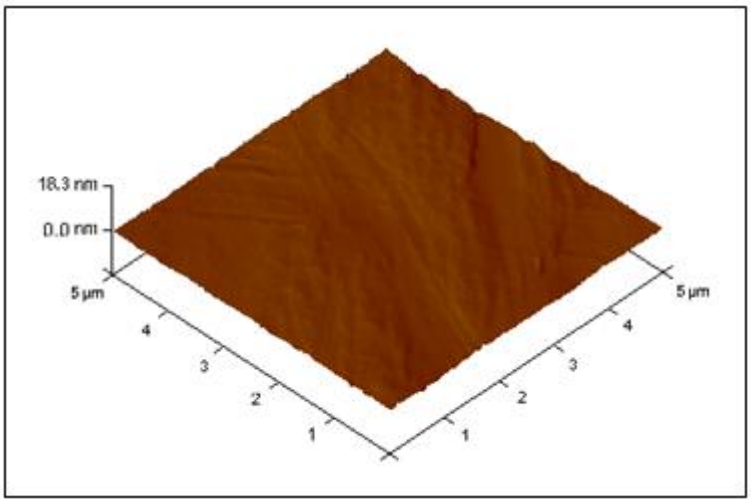

Figure 9

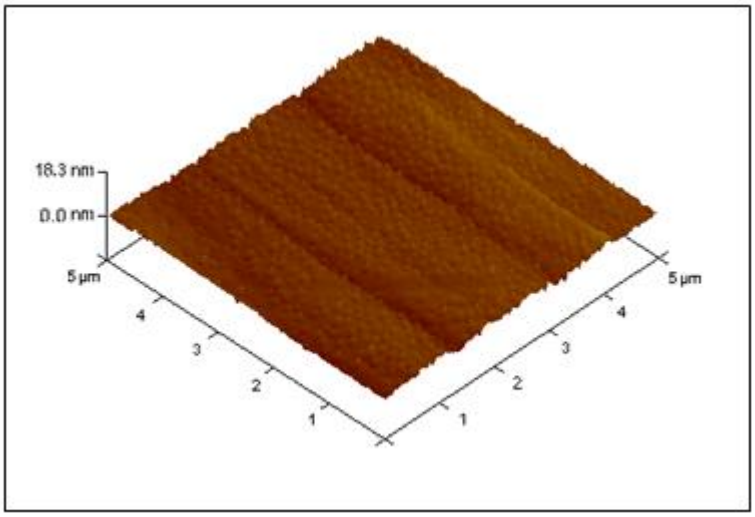

Figure 10

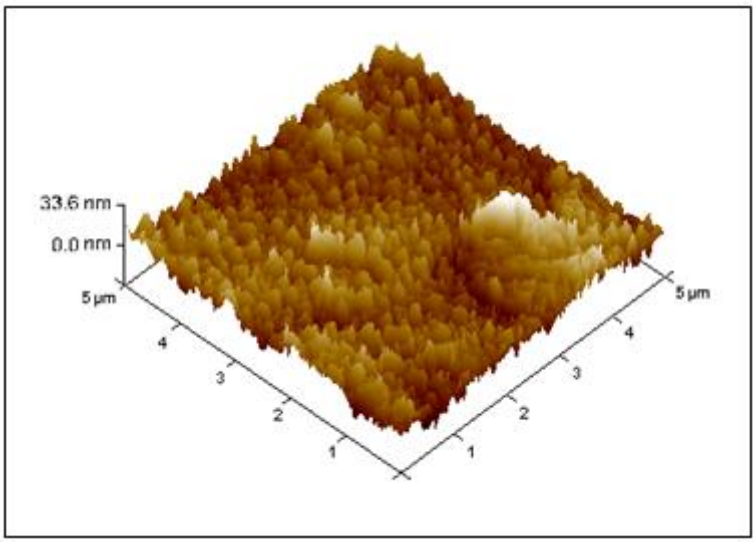

FIGURE LEGENDS

Figure 1: Schematic diagram of the experimental set-up

Figure 2: Variation of water contact angle with treatment time

Figure 3: Variation of surface free energy and its components with treatment time in air plasma. γ is the surface free energy, γ^{LW} is its dispersion part and γ^{AB} is its acid–base part. γ^{+} is the electron–donor component and γ^{-} is the electron–acceptor component of the acid-base interaction.

Figure 4: Variation of surface free energy and its components with treatment time in argon/air plasma. γ is the surface free energy, γ^{LW} is its dispersion part and γ^{AB} is its acid–base part. γ^{+} is the electron–donor component and γ^{-} is the electron–acceptor component of the acid-base interaction.

Figure 5: 2-D AFM image of untreated HDPE and profile of a water droplet on the surface, showing measured contact angle of 92.8°

Figure 6: 2-D AFM image of HDPE surface treated in air plasma for 60 s showing slightly increased roughness of the surface compared to the untreated HDPE and profile of a water droplet on the surface, showing measured contact angle of 54.0°

Figure 7: 2-D AFM image of HDPE surface treated in argon/air plasma for 60 s showing highly increased roughness of the surface compared to both the untreated HDPE and air plasma treated HDPE, and profile of a water droplet on the surface, showing measured contact angle of 46.1°

Figure 8: 3-D AFM image of untreated HDPE

Figure 9: 3-D AFM image of HDPE surface treated in air plasma for 60 s showing slightly increased roughness of the surface compared to the untreated HDPE

Figure 10: 3-D AFM image of HDPE surface treated in argon/ air plasma for 60 s showing highly increased roughness of the surface compared to both the untreated HDPE and air plasma treated HDPE

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