Surface Treatment of PET and PP by Atmospheric Pressure Dielectric Barrier Discharge for Improvement in Hydrophilicity

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Abstract. Low temperature plasmas generated under atmospheric pressure condition has been gaining popularity for the surface treatment of materials due to their many advantages over conventional methods of treatment. This paper reports the study of surface modification of Polyethylene Terephthalate (PET) and Polypropylene (PP) by using atmospheric pressure dielectric barrier discharge (DBD) to improve their hydrophilicity. The discharge was generated by using a high voltage power supply (Vpp=50 kV) operating at line frequency (50 Hz). The electrical discharge was characterized by measurement of current and voltage. The samples before and after the treatment were studied using contact angle measurements, surface free energy calculations and scanning electron microscopy (SEM). Contact angles of three test liquids: distilled water, glycerol and diiodomethane with the polymer sample were used to determine total surface free energy and its polar and dispersive components. The results showed a remarkable decrease in contact angle with plasma treated samples indicating an improvement in hydrophilicity after the treatment. SEM analysis revealed that the treatment in DBD increases the roughness of the polymer surface resulting an increase in hydrophilicity. It was also observed that addition of a small quantity of argon to the discharge can significantly enhance the surface treatment.

Keywords: DBD, Surface treatment, PET, PP, contact angle, surface energy, SEM

I. INTRODUCTION

Use of polymers is growing everyday for wide range of applications such as textiles, stationery materials, laboratory equipments, packaging, labeling, parts of automotives, etc. Although polymers have excellent bulk properties such as strength to weight ratio, resistance to corrosion, mouldability and recyclability their low hardness and poor wettabilty limits their application in several cases [1]. In particular their surface properties like hydrophilicity, adhesivity and printablility do not often meet the requirement for industrial applications. Therefore, several methods have been developed to modify their surface properties so as to extend their range of application [2, 3]. Dielectric barrier discharges (DBD) are convenient sources for the generation of non-thermal plasmas at atmospheric pressure or near atmospheric

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pressure, which avoids the higher costs of installation and maintenance associated with vacuum-based plasmas [4]. These plasmas offer convenient and environmentally friendly way to obtain surface modifications of materials by introducing new chemical groups at the surface without affecting the bulk properties. When a polymer is subjected to plasma treatment the interaction of energetic charged particles (electrons and ions) in the plasma with the polymer surface can result in the breakage of chemical bond creating free radicals in the surface. For example, the reaction between free radical and atomic oxygen can add peroxides to the surface of the polymer. The processes which involve chemical reactions between peroxides and species, like atomic hydrogen originated from the polymer or from the feed gas, can incorporate hydrophilic groups (e.g. hydroxyls) to the polymer surface [5]. The growing interest in atmospheric pressure plasmas is mainly due to the cost-effective system and possibility of continuous treatment of materials. Most atmospheric pressure DBDs reported are filamentary and hence the treatment of surface is not homogeneous. A great deal of research has been made on DBDs in recent years with an objective of obtaining homogeneous glow discharge in atmospheric pressure. The discharge conditions such as; type of the gas used, the material of the dielectric barrier, the structure of the electrode and spacing between them , frequency of power supply, and the humidity of the gas strongly determine possibility of transition of atmospheric pressure discharge from glow to filamentary nature [6,7].

In this study, an attempt has been made to compare the homogeneity of the discharge in air and air-argon mixture by analyzing the surface properties of PET and PP samples treated under these conditions. Surface characterization of the samples was performed using contact angle measurement, surface energy analysis and SEM.

II. MATERIALS AND METHODS

Generation of Discharge

Dielectric barrier discharge (DBD) at atmospheric pressure was used for the surface treatment of PET & PP films. The experimental set-up is shown in Fig. 1. The discharge was produced between two copper electrodes with dimensions 5 cm × 3.5 cm × 1 cm. The lower electrode was covered by a polycarbonate (PC) plate with dimensions 10 cm × 8 cm × 0.2 cm which served as a dielectric barrier. The inter electrode gap was adjusted by changing the position of lower electrode.

The discharge was produced using a high voltage (maximum peak-to-peak value of 50 kV) power supply operating at line frequency (50Hz). The upper electrode was connected to the high voltage power supply through a ballast resistor (20 MΩ) in series to limit the current. The bottom electrode was grounded through a shunt resistor of 10 kΩ. The discharge current was calculated by measuring the voltage cross shunt resistor. Dry ambient air and a mixture of argon and air were used as working gas. Argon with a flow rate of 2 liters per minute was used in case of argon and air mixture. The plasma treatment time was varied in a range from 5s to 60s.
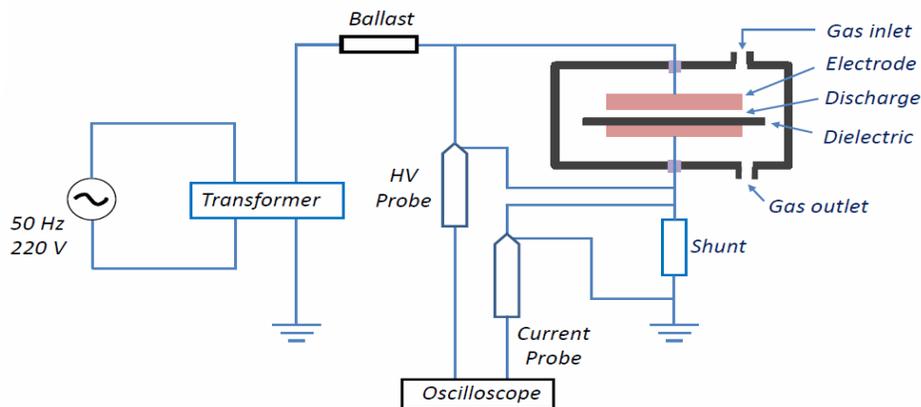
FIGURE 1. Experimental set-up used for generation of DBD and treatment of the polymer samples.

Preparation of Samples

Commercially available Polyethylene Terephthalate (PET) and Polypropylene (PP) films of thickness 0.05 mm from Goodfellow Ltd., UK were cut into sizes of 3 cm × 2.5 cm and used as samples for plasma treatment. The samples were washed in isopropyl alcohol and then washed in distilled water, ultrasonicated for ten minutes, and dried at room temperature before the treatment. The plasma surface treatment was carried out by placing the samples on the dielectric material (polycarbonate plate) in between the two electrodes.

The samples before and after the treatment were studied using contact angle measurement and the subsequent calculation of surface free energy. The morphology of the untreated and plasma treated polymer surface were investigated by using scanning electron microscopy (SEM) (Leo 500 microscope).

Contact Angle Measurement

Static contact angle measurement were made before the treatment and immediately after the treatment by dispensing 4 μl of test liquid making sessile drops on the surface of the samples. The images were recorded using CCD camera and the contact angles were measured using rame-hart contact angle goniometer, model: 200.

Three different test liquids, one apolar and two polar were required for the calculation of surface energy and its polar and dispersive components of the polymer sample using equation (1). Diiodomethane (CH_2I_2) was chosen as apolar and distilled water (H_2O), glycerol ($C_3H_8O_3$) as polar liquids. The surface energy terms were considered as Lifschitz-van der Waals (LW) and Lewis acid-base terms (AB) as represented in Eq. (1) [8-10]. The test liquids and their surface tension values with associated components can also be found in an earlier work [11].

$$\gamma_L(1+\cos\theta) = 2(\gamma_S^{LW} \cdot \gamma_L^{LW})^{1/2} + 2(\gamma_S^+ \cdot \gamma_L^-)^{1/2} + 2(\gamma_S^- \cdot \gamma_L^+)^{1/2} \quad ----(1)$$

Where γ_L, γ_L^{LW}, γ_L^+ and γ_L^- represent the surface tension of the testing liquid and its dispersive and polar components respectively. Similarly, γ_s, γ_L^{SW}, γ_S^+ and γ_S^- represent the surface energy of

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the solid and its dispersive and polar components. θ is the angle of contact between the testing liquid and the solid surface.

III. RESULTS & DISCUSSION

Electrical Characterization of the Discharge

(a)   (b)
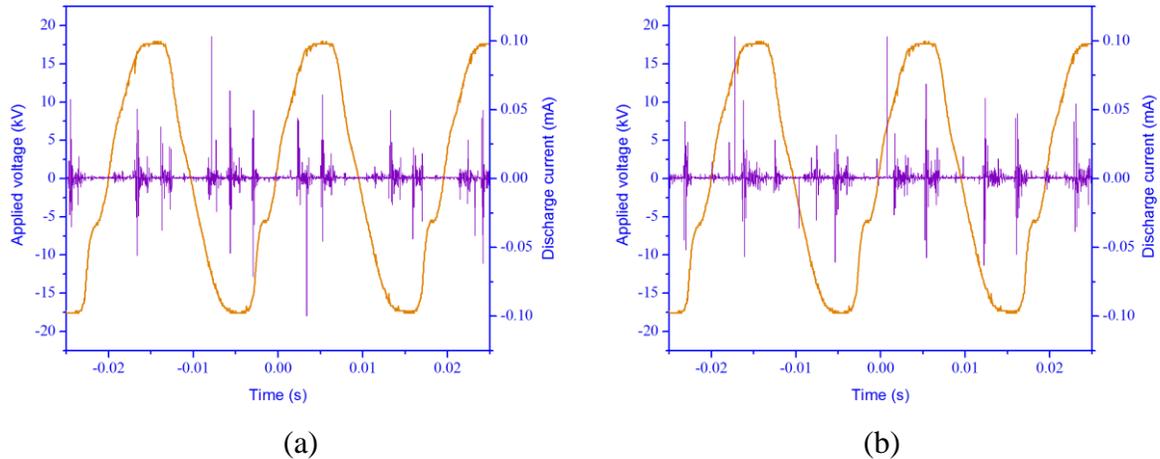
FIGURE 2. Current-Voltage waveform of the discharge in (a) air (b) air-argon discharge.

Fig. 2 (a)-(b) show the applied voltage and discharge current in DBD with air and air-argon mixture respectively. The presence of the several spikes in the current waveform in each half cycle indicates that DBD is filamentary in nature. Each spike in the waveform represents a micro-discharge channel in the space between the electrodes. A closer look of the magnitude of discharge current in each half-cycle in the figure reveals that the discharge is more prominent and uniform with mixture of argon compared to air alone. Power used for the discharge is less than a watt because the current was largely limited by using ballast resistor of 20 Mohm in order to avoid the damage of thin polymer samples during the treatment.

Contact Angle on Polymers

(a)   **(b)**
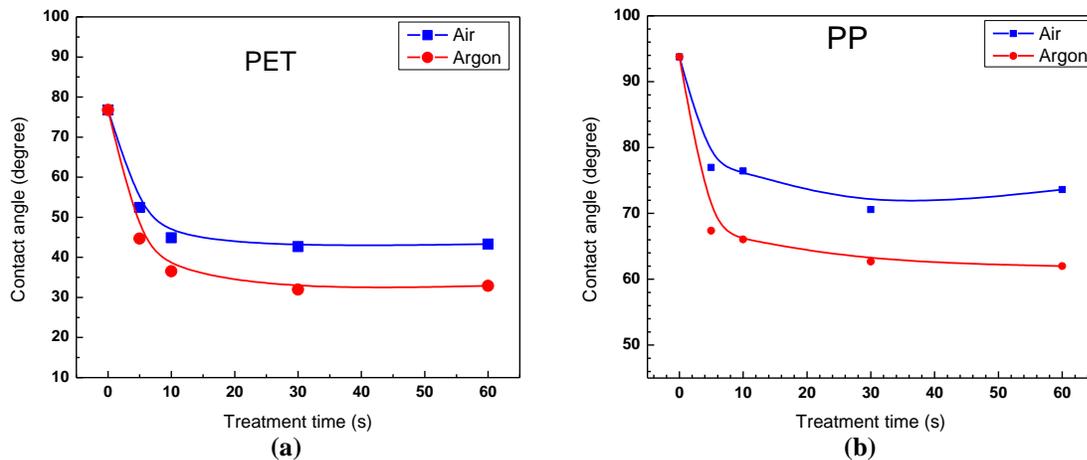
FIGURE 3. Contact angle on (a) PET and (b) PP surface as a function of treatment time in air/argon discharge.

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Fig. 3 (a)-(b) shows the contact angle on the surface of PET and PP treated in DBD in air or air-argon medium. It is evident from the Fig. 3(a) that contact angle decreases rapidly for treatment time up to 10 seconds which indicates an increase of wettability in the PET surface induced by the treatment. The contact angle observed is found to change from 76.7° for the untreated sample to the minimum values of 44.8° after 10 seconds of treatment in air, and 36.5° after 10 seconds of treatment in argon-air mixture. Similarly, for PP, the contact angle is found to change from 93.7° for the untreated sample to the minimum values of 76.4° after 10 seconds of treatment in air and 66.0° after 10 seconds of treatment in argon-air mixture.   It is interesting to note that addition of argon in the discharge can have significant effect on the surface properties as evident from the Fig.3. The contact angles on the sample treated in air-argon discharge is nearly 10° lower compared to the sample treated in air DBD. The discharge in air with a mixture of argon can have active species (O, OH, NO, UV radiation) which can react with the broken chain of polymer in the surface resulting the incorporation of polar functional groups on the surface which might be the main cause for the decrease in water contact angle. These results are in agreement with our earlier studies made on other polymers [12].

Surface Energy of the polymers

Surface energy and components of PET and PP after different treatment time in plasma were calculated from the contact angles as described above. The results are shown in Table 1 and 2 respectively. The last column of the table shows the data in terms of polarity (γ^{AB}/γ^{Tot}). It is seen that all the samples have significant values of γ^{LW}. It is interesting to note that the polarity of the samples increases appreciably with the treatment time.

TABLE 1. Components of the surface free energy of PET after treatment in plasma for different time.

Treatment(s)	γ^{Tot}	γ^{LW}	γ^{AB}	γ^{+}	γ^{-}	γ^{AB}/γ^{Tot}
0	44.5	43.1	1.4	0.08	6.3	0.03
5	52.4	42.8	9.6	0.79	29.1	0.18
10	55.4	43.3	12	1	34.7	0.22
30	55.3	42.9	12.3	0.96	39.5	0.22
60	56.2	42.4	13.8	1.3	37.3	0.24

TABLE 2. Components of the surface free energy of PP after treatment in plasma for different time.

Treatment (s)	γ^{Tot}	γ^{LW}	γ^{AB}	γ^{+}	γ^{-}	γ^{AB}/γ^{Tot}
0	36.7	36	0.77	0.08	2	0.02
5	42.9	40.5	2.3	0.09	14.3	0.05
10	42.8	40.6	2.2	0.08	15.7	0.05
30	42.6	41.3	1.3	0.02	19.6	0.03
60	43.8	41.8	2	0.05	19.3	0.04

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The effect of the plasma treatment on the surface energy component can be better understood from Fig. 4 and Fig. 5. Before the treatment, γ^{LW} accounts for 96.85 % of $\boldsymbol{\gamma^T}$ while γ^{AB} accounts for only 3.16 % of γ^T. It is interesting to note that the relative magnitude of γ^{LW} and γ^{AB} alters appreciably after the treatment changing γ^{LW} to 81.9% and γ^{AB} to 18.1%. However, for PP, the change is not as prominent as for PET as evident from Fig. 5. This difference in the effect   of plasma treatment on surface energy of PET and PP may have been caused due to the fact that PET consists of oxygen in its structure whereas there is no oxygen in PP.


(a)	(b)
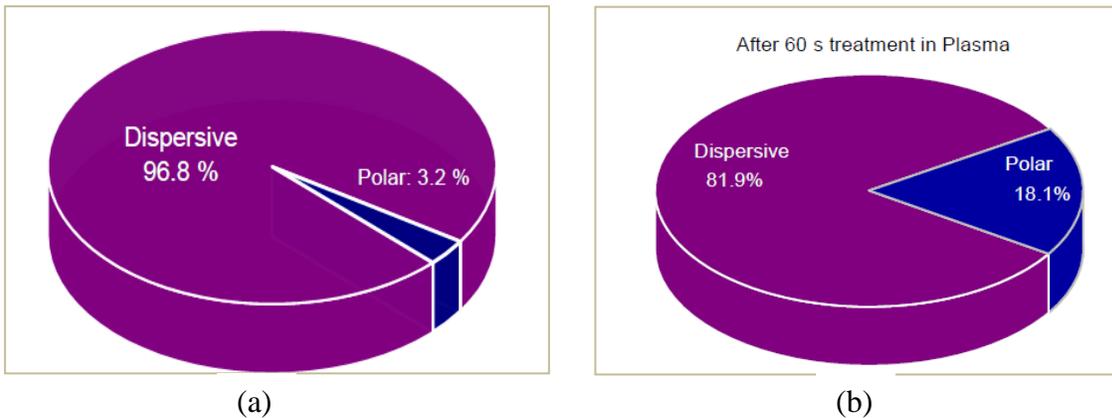
FIGURE 4. Polar and dispersion component of Surface energy of PET before (a) and after treatment (b) in argon plasma for 60s Blue color represents polar part and the magenta represents the dispersive part of the surface energy.



(a)	(b)
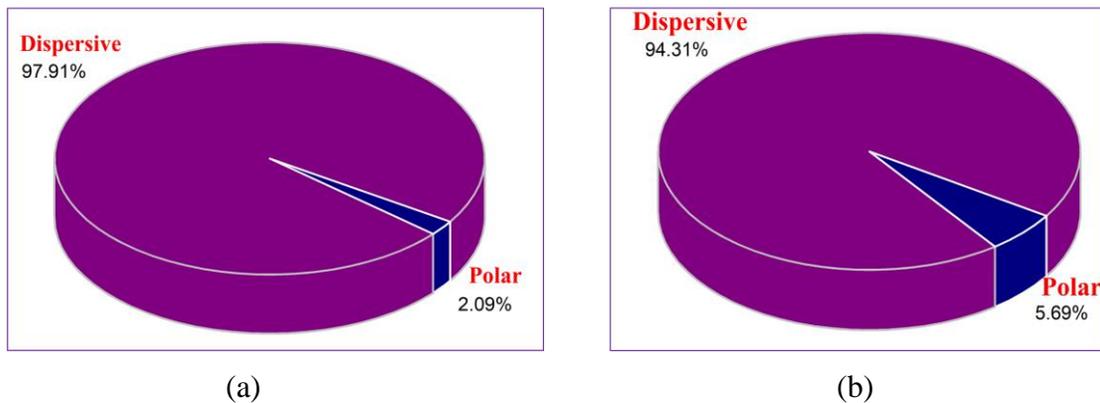
FIGURE 5. Polar and dispersion component of surface energy of PP before and after treatment in argon plasma for 60s. Blue color represents polar part and the purple represents the dispersive part of the surface energy.

SEM analysis

Considerable changes in the surface roughness was detected on the sample treated in DBD generated in air with a mixture of argon as evident from SEM images shown in Fig. 6 (a) – (f). In order to compare the effect of treatment environment on surface roughness, the samples were treated in DBD in air or air-argon mixture. It can be seen from the figures that the treatment in DBD with mixture of argon leads to higher roughness. The surface morphology of the untreated samples in Fig 6 (a) and 6 (d) appear comparatively smooth. It can be seen that the surface is etched/sputtered uniformly and surface roughness is increased significantly after the treatment. DBD with air-argon mixture as working gas can generate a wide range of species (atomic
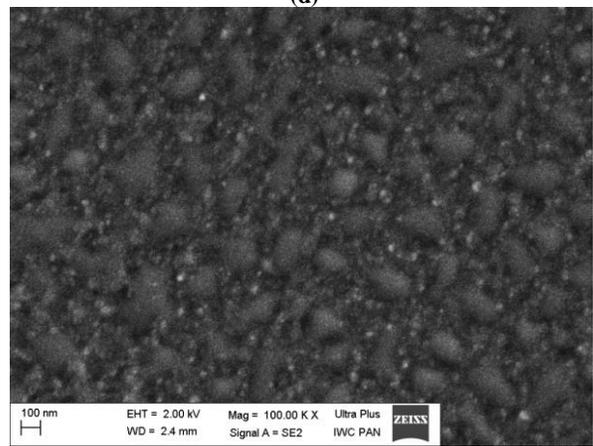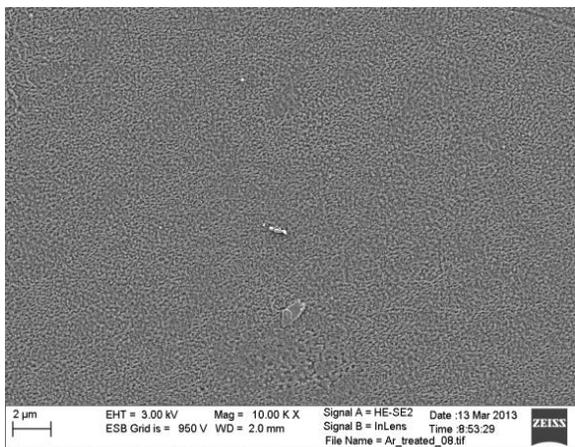
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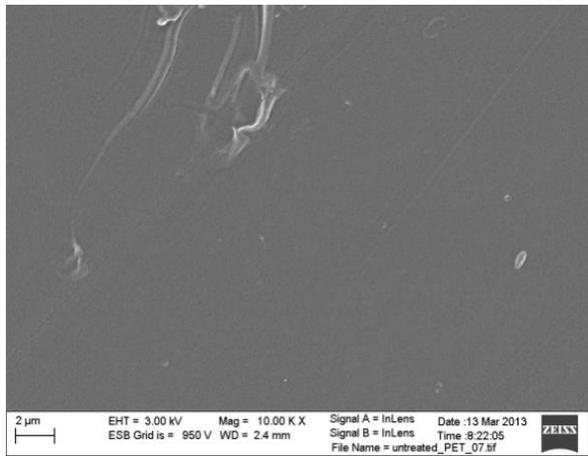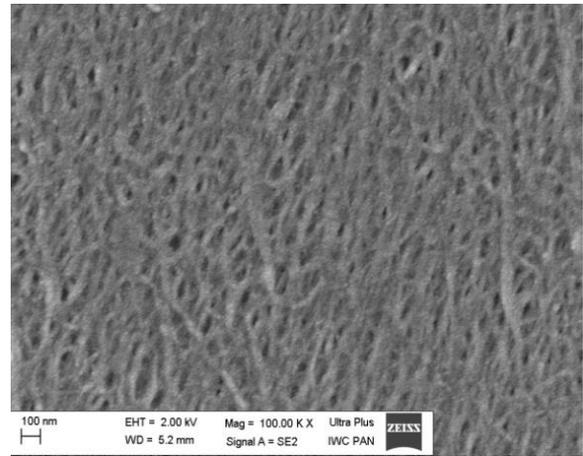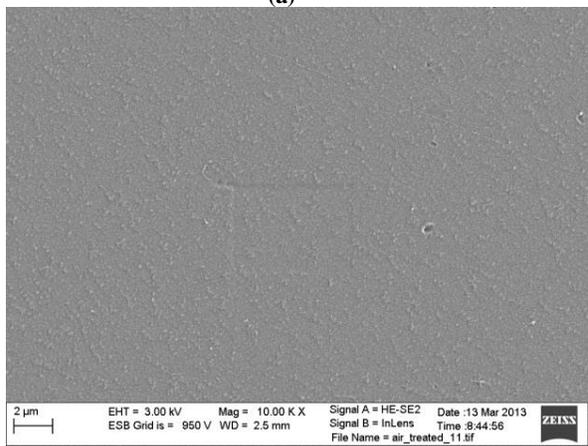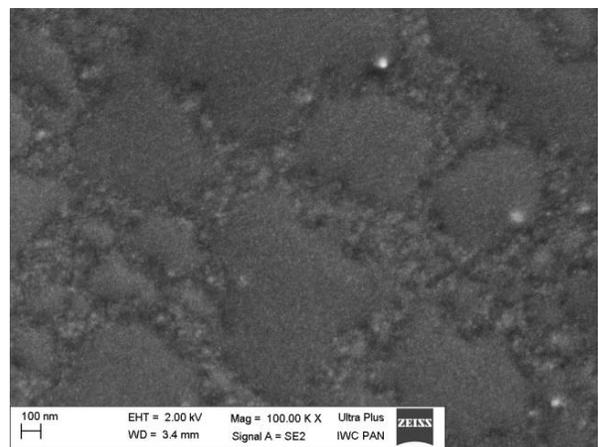
FIGURE 6 SEM image of (a) untreated PET (b) treated in air DBD (c) treated in air-argon DBD. Right column (d) untreated PP (e) treated in air plasma and (f) treated in air-argon DBD. The plasma treatment time was 60s.

oxygen, argon ion and excited atoms, NO, UV, free radicals, ozone) in the discharge regime. Therefore, the polymer surface under the action of plasma is exposed to highly reactive environment leading to the modification of surface through plasma chemical reactions. One important process during the treatment could be the breaking of polymer bond which causes the etching of the surface resulting the change in surface morphology.

IV. CONCLUSION

Surface modification of PET and PP with DBD generated by line frequency power supply and operating at atmospheric pressure was studied. Contact angle measurement and subsequent analysis of surface energy showed that the ratio of the polar component to total surface energy (γ^{AB}/γ^{T}) of the polymers was altered after the treatment. Moreover, the change in this ratio was more prominent in the case of PET compared to that of PP. SEM images revealed that the polymer treatment was homogeneous and the surface roughness of the sample treated in DBD with air-argon medium was higher compared to the sample treated in DBD with air.

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