Characterization Of Dielectric Barrier Discharge (DBD) Produced In Air At Atmospheric Pressure And Its Application In Surface Modification Of High-Density Polyethylene (HDPE)

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The low surface energy of HDPE limits its industrial uses as it is not suitable for printing and adhesion. The main aim of this work is to improve the wetting properties of high-density polyethylene (HDPE) using air dielectric barrier discharge (DBD) operating at the line frequency (50 Hz). The estimation of electron temperature and electron density has been done by electrical and optical methods. The surface roughness of the control and plasma treated polymer film is analysed by contact angle (CA) measurement, surface energy measurement and scanning electron microscope (SEM) analysis. The contact angle was found to be suppressed from $93.1^0 \pm 2.0^0$ to $64^0 \pm 1^0$ after 10 sec of plasma treatment which implied that the surface property had changed to a hydrophilic state caused by an increase in the surface roughness.

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I. Introduction

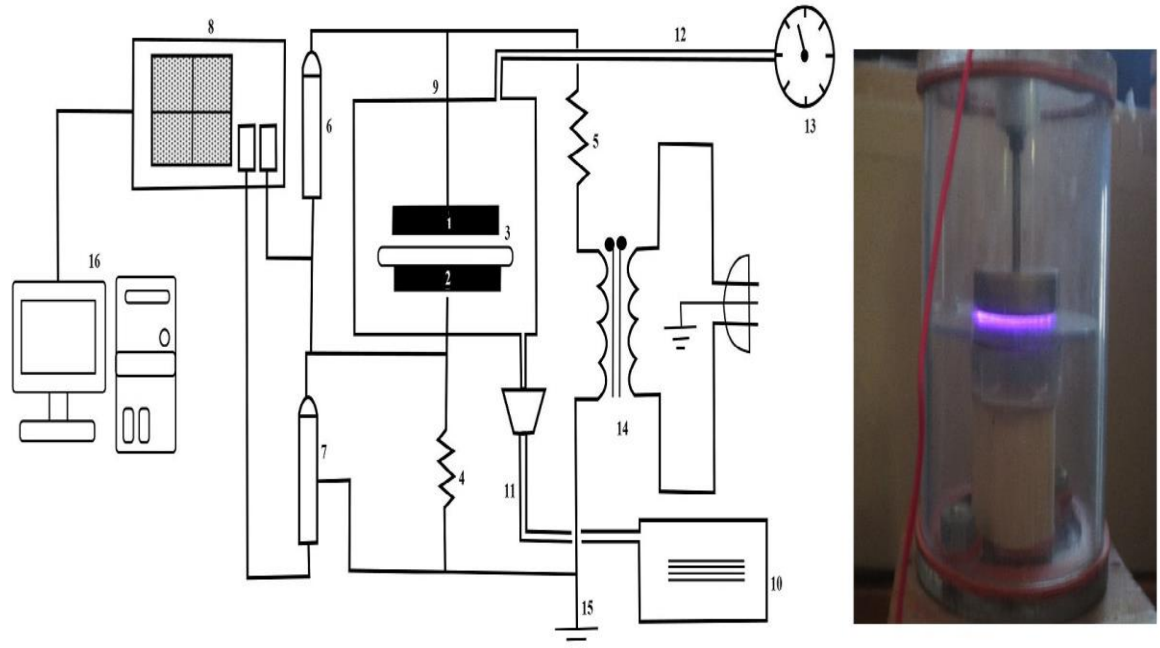
High Density Poly Ethylene (HDPE) is a recyclable thermoplastic polymer made from petroleum product which is the most versatile plastic materials around, and used in a wide variety of applications, including plastic bottles, toys, soda bottles, trash cans, traffic cones bleach bottles, cutting boards, and piping [1]. The main reason for its wide range of applications is its superb characteristics viz., high chemical resistance, good mechanical properties (high flexibility, high tensile strength and ease of material processing), high recycling potential and low cost [2,3]. However, the surface energy of HDPE is quite low due to the absence of polar functional groups in PE molecular chains [4,5], which limit their potential application in various fields. As a result, its surface properties such as hydrophilicity, adhesivity and printability do not often meet the requirement for industrial applications. [5]. In order to spread its uses in different sectors, its surface modification is necessary. Different physical (dry) as well as chemical (wet) methods have been in practice since the decade for the modification of the polymer surface. However, the chemical method is water-wasting and environment polluting. In contrast, the physical method has attracted much attention in recent years [6-9].

Plasma treatment is one of the versatile physical methods for surface modification of polymers as it does not leave any chemical residue on the treated surface [10-12]. Because of the heat sensitivity of the polymer, non-thermal plasma also called cold plasma is suited for its surface modification and processing. Non-thermal plasma has the ability to modify the surface of the polymer by adding specific functional groups without altering the bulk properties of the material [13-15]. But the generation of non-thermal plasma in low pressure and high frequency needs a vacuum system which increases the budget of the operation and also makes it inconvenient for large scale treatment.

Thus, in order to minimize the operation cost and elaborate its uses in industrial level, the use of atmospheric pressure plasma is grooming day by day [16-18]. In this paper, the effect of pre-treatment of the polymer surface with non-thermal plasma produced at atmospheric pressure using line frequency (50 Hz) has been discussed. Non-thermal plasma generated by ac voltage source operating at the line frequency is used to modify the surface of the HDPE sample. The surface properties of the treated materials were studied in terms of contact angle and surface energy measurements. It was observed that both the contact angle and surface energy of the material changed after being treated with the non-thermal plasma.

II. Materials and Methods

Fig. 1 shows the typical experimental set up and nature of the discharge used for the present study. The reactor system consists of a transparent cylinder of height 10 cm, diameter 10 cm and thickness 0.5 cm. An orifice is made on the cylinder and a fibre optic cable is inserted there and sealed.



(1,2) Electrodes (3) Dielectric Sheet (PC) (4) Ballast Resistor (5) Shunt Resistor (6) Voltage Probe (7) Current Probe (8) Oscilloscope (9) Reaction Chamber (10) Vacuum Pump (11,12) Pipes (13) Pressure Gauge (14) High Voltage Transformer (15) Ground (16) Computer Interfacing

Figure 1: Schematic diagram of the experimental setup and image of the discharge.

Both the electrodes used in the study are made of brass (5.1 cm × 5.1 cm × 1.0 cm). A polycarbonate sheet of 2 mm thickness is inserted between the two electrodes which serves the purpose of the dielectric barrier. The reactor consists of two pipes. One of the pipes is connected to a vacuum pump while the other pipe is connected to the analogue pressure gauge. The reactor is designed in such a way that it can be made to operate in both the atmospheric and reduced pressure (as low as 5300 Pa). For all DBD treatments the gap between the electrodes was fixed at 3.5 mm. The ac voltage applied to the reactor was measured by using a high- voltage probe (PINTEX HVP-28HF) and monitored on a digital oscilloscope (Tektronix TDS 2002, 60MHz). The attenuation ratio of the high voltage probe is 1000:1. For displaying the waveform of the discharge current on the oscilloscope, the reactor lower electrode was grounded through a current measuring resistor of 10 KΩ. A spectrometer of Ocean Optics (USB 2000+) has been used for the measurement of emission spectra. In this work, the operating ac voltage and frequency were maintained at 11.76 kV rms and 50 Hz respectively. Prior to the treatment, HDPE samples of dimension (50 mm × 15 mm × 0.05 mm) provided by Goodfellow, UK, were ultrasonically cleaned in distilled water for 20 minutes. To get rid of the organic contamination, the samples of HDPE were rinsed in methanol for 10 minutes and then dried at room temperature in a clean environment.

The contact angle between a test liquid and the polymer surface was obtained by the sessile drop method on a standard Rame-Hart goniometer, model 200 using the DROP Image software. The contact angle assessments were performed within 30 min after the treatments. All plasma treatments were administered in air at atmospheric pressure and ambient temperature. The contact angle measurement was done at four different locations of the same samples and the average value of the contact angle thus obtained was used for the surface energy calculations. The maximum error in the contact angle assessments did not exceed 2%. In this work, LEO (500) /Zeiss Field-emission scanning electron microscope (SEM) was used to examine surface morphology.

III. Results and Discussions

III.a) Electrical Characterization

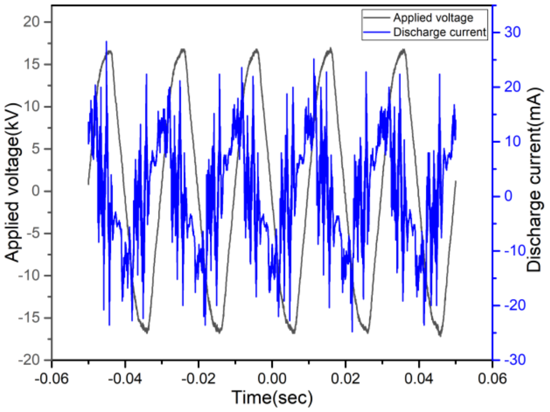


Figure 2: Typical current and voltage waveforms for 50 Hz DBD

Fig. 2 shows the typical current and voltage waveform of DBD generated in air at atmospheric pressure condition. The current peak appears on both the rising and falling of the discharge voltage. The current peaks on the rising part correspond to positive polarity where some of the charges accumulate on the dielectric barrier and the current peaks of the falling part correspond to reverse negative polarity in which the accumulated charges are changed. The current density J was obtained by dividing the discharge current, I by the cross-sectional area of plasma, A.

$$J = \frac{I}{A} \qquad (1)$$

The average electron density n_e can be calculated from the following equation [19,20].

$$n_e = \frac{J}{e\mu_e E} \qquad (2)$$

In our case, the cross sectional area of the plasma = cross sectional area of the electrodes = 20.41 cm², Discharge current = 22.8 mA, Applied Voltage = 11.76 kV (rms), inter-electrode distance (d) = 3.5 mm = 0.35 cm, electron mobility $\mu_e \approx 552$ cm² [20, 21]. The electron mobility can be calculated as follows:

$$\mu_e = \frac{e}{m\nu_m} \qquad (3)$$

Here, e represents the electronic charge, m represents the mass of the electron and ν_m represents the effective collisional frequency.

The value of effective collision frequency for nitrogen is found to be [21]:

$\nu_m = 4.2 \times 10^9\ s^{-1}\ torr^{-1}$

Substituting these values in Eq. (2), the electron mobility is estimated as

$$\mu_e = 1.67 \times 10^{15} \times \frac{1}{3.192 \times 10^{12}} \qquad (4)$$

$$\rightarrow \mu_e \approx 552\ cm^2/Vs \qquad (5)$$

Using all these values in Eq. (2), the electron density was found to be in the order of 3.7×10^8 cm^{-3}.

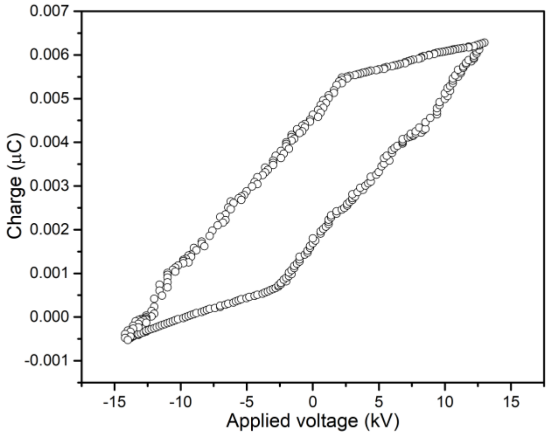


Figure 3: Lissajous figure of the discharge at atmospheric pressure condition

Fig. 3 shows the voltage-versus-charge plot or the so-called Lissajous figure of the discharge operating using line frequency at atmospheric condition. The energy dissipated per cycle is found to be 0.4184 mJ per cycle.

III.b) Optical Characterization of the discharge

Fig. 4 shows the spectra of the discharge and their corresponding intensities at atmospheric pressure condition.

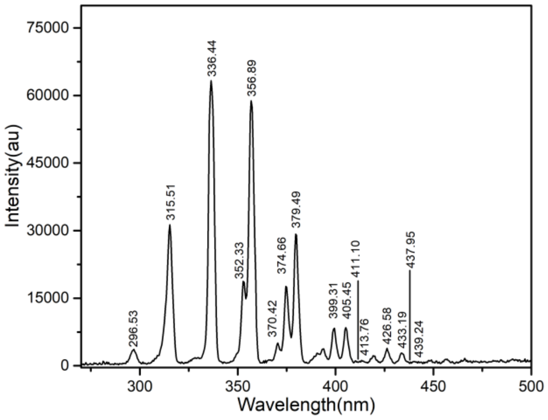


Figure 4: Spectra of the discharge at a frequency of 50 Hz in an atmospheric

The line intensity ratio method was employed for the estimation of electron temperature [22,23]. In this method four suitable lines; two for N I (413.7640 nm, 439.241 nm) and two for N II (411.1039 nm, 437.9585 nm) were chosen from spectral lines of Nitrogen obtained from the discharge.

$$\frac{R_1}{R_2} = \frac{\frac{I_1}{I_2}}{\frac{I_3}{I_4}} = \left(\frac{A_{pq}}{A_{rs}}\right)\left(\frac{g_p}{A_r}\right)\left(\frac{\lambda_{rs}}{\lambda_{pq}}\right)\left(\frac{A_{uv}}{A_{xy}}\right)\left(\frac{g_u}{g_x}\right)\left(\frac{\lambda_{xy}}{\lambda_{uv}}\right)$$

$$exp\left[-\frac{E_p - E_r - E_x + E_v}{kT_e}\right] \quad (6)$$

Here, in Eq. (6), R is the ratio of the intensity of two lines, I is the intensity of the spectral line, A_{ij} is the transition probability of the transition i → j, g_i is the statistical weight of the upper level, λ is the wavelength of the line radiation, E_i is the energy of the upper level, k is the Boltzmann constant and T_e is the electron temperature. The values of λ and I are obtained from the observation, and the values of A_{ij}, g_i and E_i are obtained from the National Institute of Standards and Technology (NIST) Atomic Spectra Database [24].

Tab. 1 shows the corresponding values of the ratio of the intensity of the spectral lines with the change in electron temperature.

Table 1: Electron temperature and its corresponding intensity ratio

Electron Temperature (T_e)	**Ratio of intensity of Spectral Lines (R_2/R_1)**
0.8	2.00173
0.9	1.05178
1.0	0.62855
1.1	0.41248
1.2	0.29038
1.3	0.21576
1.4	0.16727
1.5	0.13415
1.6	0.1106
1.7	0.09327
1.8	0.08017
1.9	0.07001
2.0	0.06197

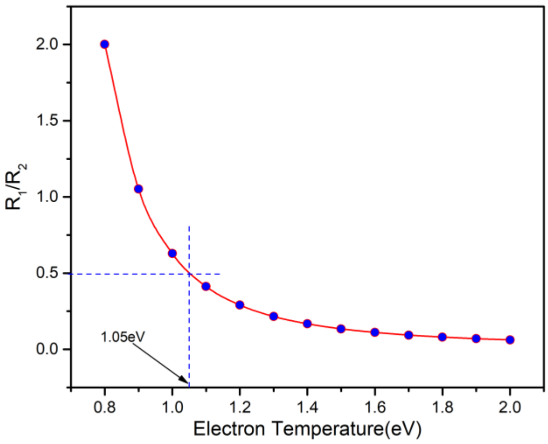


Figure 5: Plot of R_1/R_2 as a function of T.

From Fig. 5, the electron temperature is found to be about 1.05 eV. This temperature is favourable for the surface modification of the polymeric films as the discharge used for material processing typically have densities of 10^9-10^{12} /cm^3 and electron temperature in the range 1-10 eV [25,26].

III.c) Polymer wettability

The wettability of polymer indirectly indicates its susceptibility to molecular interaction with the liquid phase and the presence of polar groups on the surface. WCA measurements can provide some qualitative information about the polymer surface modification [27].

For an ideal, smooth and homogeneous surface, the water contact angle and surface free energy are measured at the equilibrium according to the Young's equation and Owens Wendt Kaeble methods respectively [28,29].

$$cos\theta = \frac{\gamma_{sv}-\gamma_{sl}}{\gamma_{lv}} \qquad (7)$$

Where, γ_{sv} is the surface free energy of the solid substrate, γ_{sl} is the interfacial tension (interfacial free energy) between the solid and the liquid and γ_{lv} is the surface tension of the liquid.

For two liquids j and k,

$$\gamma_{li}\left(1+cos\theta_j\right) = 2(\gamma_{lj}^{d}\gamma_s^{d})^{1/2} + 2(\gamma_{lj}^{p}\gamma_s^{p})^{1/2} \qquad (8)$$

$$\gamma_{lk}\left(1+cos\theta_j\right) = 2(\gamma_{lk}^{d}\gamma_s^{d})^{1/2} + 2(\gamma_{lk}^{p}\gamma_s^{p})^{1/2} \qquad (9)$$

Using the values of the surface tension, polar and dispersion components of the test liquids, components of surface free energy of the solid, i.e. $\gamma^p{}_s$ and $\gamma^d{}_s$ can be determined by solving the Eqs. (8) and (9). The sum of these two quantities eventually gives the total surface energy of the solid.

The influence of treatment time on the wettability was investigated, using a Rame Hart contact angle goniometer (model 200) using two test liquids (water and glycerol) on the surface of the HDPE.

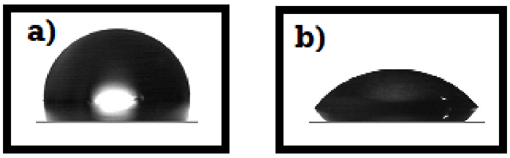


Figure 6: Water contact angle of control (a) and plasma treated(b) HDPE thin films for

Fig. 6 shows the images of the untreated and plasma treated high density polyethylene films for 60 seconds. When polymers are exposed to plasma, basically two phenomena occur simultaneously. First is etching of the polymer surface through the reaction of atomic oxygen with the surface carbon atoms, giving volatile reaction products. Second is the formation of oxygen functional groups at the polymer surface through the interaction between the active species in plasma and the surface atoms [30].

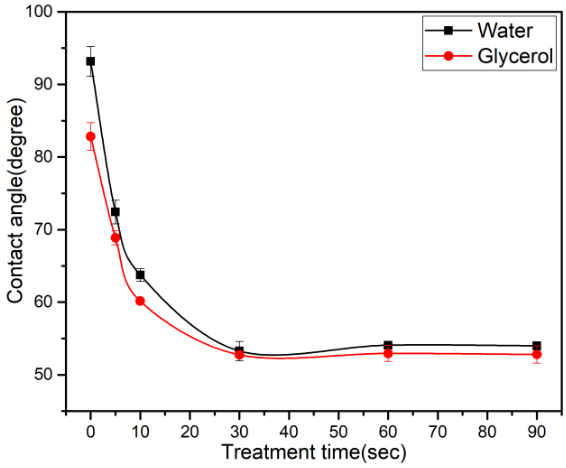


Figure 7: Variation of the contact angle as a function of treatment time.

Fig. 7 shows the water contact angle (WCA) of DBD-treated HDPE films as a function of treatment time. Here, the water contact angle of the untreated sample of HDPE was found to be 93^0±2^0. After 10 sec of plasma treatment, the water contact angle was significantly decreased to 64^0±1^0 as depicted in Fig. 7 exhibiting that DBD treatment can be used for improving the surface wettability. This might be due to the incorporation of new oxygen related functional groups on the surface. However, the extension of the treatment time did not result in further improvement of polymer hydrophilicity and the WCA of plasma modified HDPE attained saturation value of around $54.1^0 \pm 0.3^0$. This might suggest that the etching and the oxidation come to a saturation when the surface of samples are exposed to the air-DBD [30,31].

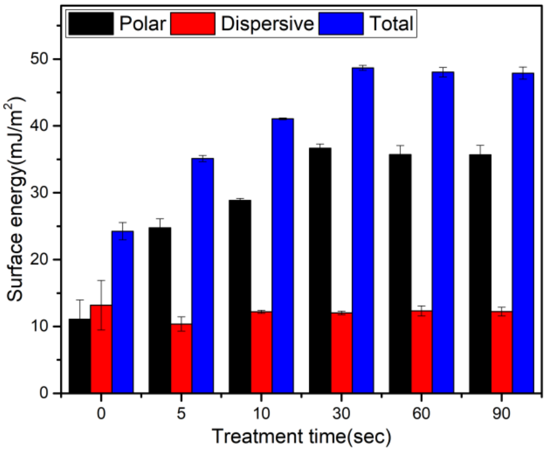


Figure 8: Variation of the surface free energy as a function of treatment time.

Fig. 8 shows the variation of surface energy as a function of treatment time. The surface energy of the untreated HDPE film was 24±1 mJ/m^2. Plasma treatment appears to increase the surface energy up to 30 seconds exposure time; and thereafter tending to saturate. This may be due to the lack of any change in the oxygen content incorporated into the surface, as the exposure time increased. Finally, the surface energy saturates at 48±1 mJ/m^2. Similar trend is observed for the polar component. It might be due to the incorporation of polar groups such as C=O, -OH, -COO etc. [31,32]. The dispersive component almost remains constant. This component does not have any contribution to increase the wettability of HDPE films. Hence the increase in surface energy is mainly due to the incorporation of polar groups onto the HDPE surface. The details of this oxidation, leading to the enhanced hydrophilicity observed has been assessed by ATR-FTIR, XPS analyses by various researchers [30-32].

III.d) Ageing effect:

One of the most important challenges in plasma processing is to achieve a long-lasting treatment effect. The change in the contact angle of the 60 seconds plasma treated HDPE films was monitored for 10 days. Distilled water was only used for the measurement of contact angle.

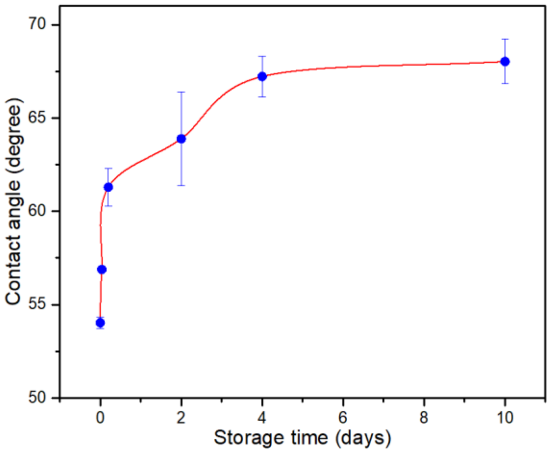


Figure 9: Variation of contact angle with storage time

It is seen that the water contact is found to be changed more rapidly for the first few hours and then changes very slowly to reach a stable value of about 68^0 which is still smaller than the untreated HDPE films. The change in the contact angle might be due the change in the polymer chain motion, reorientation of the polar group into the polymer bulk or only within the modified surface. The decay in wettability might be due to the reduction of the hydrophilic functional groups and partially due to hydrocarbon re-adsorption.

III.e) Surface morphology:

During plasma treatment, energetic plasma species bombard and cause etching of HDPE films surface, leading to an increase in the surface roughness [32,33].

Fig. 10 shows the SEM morphology of untreated and plasma treated HDPE films at 60 seconds. The morphology of the control sample is smoother than that of the plasma-treated one. The gradual increment in the particle grain size with the image scan area can be realized. The increase in the surface roughness of the HDPE film could have been caused by the excited reactive species from the discharge plasma in the ambient air. These highly reactive species could have etched and roughened the film surface. This increase in the surface roughness might be responsible for the decrease in the contact angle.

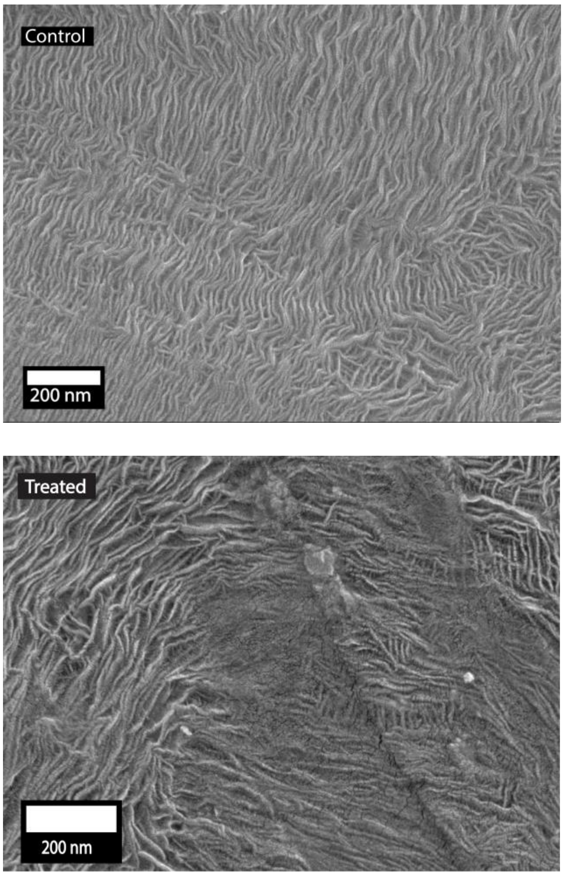


Figure 10: SEM images of the control(untreated) and Plasma treated HDPE

Several other authors have also reported a similar roughness trend for the plasma-treated polymers [31-35].

IV. Conclusions

In this work, an atmospheric pressure plasma has been used to modify HDPE film surfaces using line frequency (50 Hz). Electron density and temperature of the discharge were found to be $3.7\times10^8/cm^3$ and 1.05 eV respectively. The plasma treatment can greatly change the surface chemistry as well as morphology of HDPE films. The polar functional groups generated due to plasma treatment on the surface of HDPE films cause decrease in contact angle and rise in surface energy. The reduction of the water contact angles on treated HDPE films as compared to the untreated (control) one shows the strong increased wettability induced by the air-DBD even after such short treatment time. This behaviour can be attributed to strong surface oxidation. The molecular oxygen which is in contact with the air is activated, ionized and dissociated in the discharge to give extremely reactive oxygen species which can readily react with the HDPE films. Ageing effect showed that the so-called hydrophobic recovery of the HDPE films occurred as the storage time increased. The results from the SEM measurement showed a gradual increase in the surface roughness of the plasma treated surface with treatment time. The morphological changes made on the surface of HDPE films lead to increase in hydrophilic properties. It is further seen that there is a direct relationship between the roughness of the surface and the wettability. The results from sessile drop examination confirmed that contact angle of HDPE decreases as surface roughness increases. The effect will find attraction on industrial applications. In the present study, it is evident that more than 40% decrease in the value of water contact angle is achieved in just 30 second of exposure to plasma. Therefore, quick hydrophilization of HDPE using cost-effective plasmas devices could be the novelty of the present work. Thus, the results from our experiment showed that the atmospheric pressure plasma treatment operating at 50 Hz could be a cost-effective technology to improve the wettability of HDPE films as compared to rf-sources operating at high frequencies.

V. Acknowledgments

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