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Effect of electrode geometry on surface modification of polyethylene terephthalate by dielectric barrier discharge produced in air at atmospheric pressure

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Abstract

This paper presents the effect of electrode geometry on the surface modification of polyethylene terephthalate (PET) as a function of distance using 50 Hz dielectric barrier discharge at atmospheric pressure conditions. The polymer samples were treated with a Gaussian shaped electrode using a 13 kV power supply at line frequency for 1 minute. The results demonstrated that plasma treatment with a Gaussian shaped electrode improves the sample's surface wettability significantly. It is seen that there is a remarkable decrease in contact angle at the center of the sample and a relatively smaller amount of decrement away from the center of the sample.

Keywords: Atmospheric pressure plasma; Electron density; Electron temperature; Polymer; Wettability

1. Introduction

Plasma treatment of polymers has been widely used in the surface modification of polymeric materials to increase its material adhesion and improve compatibility [1,2]. Among various methods to modify the surface properties of polymeric materials, plasma treatment has attracted much attention in recent decades because of its versatility, low cost, and ease of operation [3]. Though a gas flow is not required, non-thermal plasma is usually generated by providing a gas at low flow rate. Often, it is convenient to generate the plasma at atmospheric pressure. One of the successful approaches to obtain non-thermal plasma at air pressure is the utilization of dielectric barrier discharge (DBD) [4,5]. Polyethylene terephthalate (PET) polymer is being used nowadays because of its superior performance, low cost, good breakage resistance, transparency, low inflammability, and its high strength to weight ratio [6]. However, its low scratch resistance, degradation by UV radiation, and low hardness makes the surface modification necessary [7]. Due to their low surface energy, poor chemical reactivity, and weak cohesion layer on the surface, it is necessary to enhance the surface properties of polymers without changing their bulk properties [8].

Most of the polymers like PET, PP, PA, PC, etc. treated industrially are heat sensitive, so treating them with hot plasma doesn't yield good results. Dielectric barrier discharge (DBD) is one of the most widely used methods for generating non-equilibrium plasmas, and it has been extensively studied and widely used for various industrial applications [9]. A DBD is generated between two metallic electrodes in which at least one of them is roofed by a dielectric barrier, with an AC high voltage applied to those electrodes. The dielectric barrier limits the discharge current, preventing the transition of the discharge to an arc discharge to make sure that a stable non-equilibrium plasma is often generated within the discharge regime, which is suitable for surface modification of material. The process of surface modification within the polymer surface is greatly affected by the geometry of the electrodes [10].

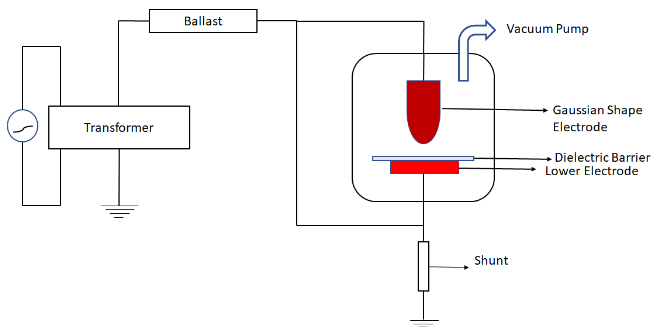

Figure 1: Schematic diagram of the experimental setup.

In this paper, electron density at atmospheric pressure (DBD) in the air environment is measured by the current density method, whereas the electron temperature is measured by the line intensity ratio method. The change in hydrophilic properties of the sample has been studied by contact angle measurements.

2. Experimental setup

The general view of the experimental set-up is shown in Fig. 1.

Plasma is generated between two non-symmetric parallel electrodes, one of which is a circular brass electrode having radius of 5.5 cm and 1 cm thickness. The other is a Gaussian-shaped copper electrode. A polycarbonate sheet of 0.20 cm thickness is used as a dielectric barrier which limits the current. The total gap between the two electrodes is 0.35 cm. The upper Gaussian-shaped electrode is movable while the lower electrode is fixed on a ver-

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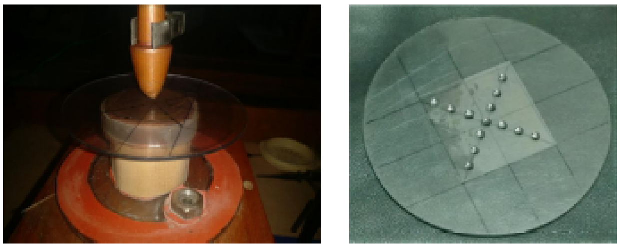

Figure 2: Photograph of the experimental setup and the water droplets on PET surface.

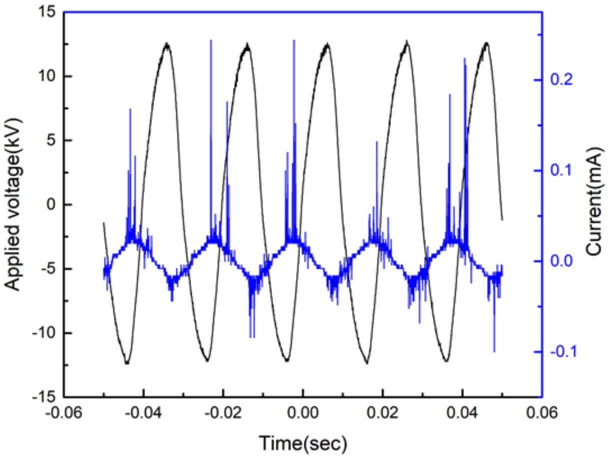

Figure 3: Current voltage graph at an applied voltage of 13 kV.

tical scale to adjust the electrode gap in atmospheric conditions. The whole setup and arrangement are made in a such a way that it can be operated in both atmospheric and reduced pressure conditions. The discharge is generated via a line frequency (50 Hz) high voltage power supply of 13 kV which is simply a step-up transformer with a high-tension side to a low-tension side ratio of 78.26. The lower electrode of the reactor system is connected to the high voltage power supply through a ballast resistor (20 MΩ) in series to limit the current. The upper electrode is grounded through a shunt resistor across which the discharge current is measured. Electrical characterization of the discharge is done by the measurement of current and voltage waveforms using a TEKTRONIX TDS2002 oscilloscope with a current probe and a PINTEX HVP-28HF voltage probe. The voltage probe has an attenuation ratio of 1000:1. Additionally, optical characterization of the discharge has been done with the help of an optical emission spectrometer (USB 2000+, Ocean Optics).

Fig. 2 shows the experimental set up and the water droplets on the polymer surface. Prior to treatment, PET samples with dimensions (4.0 cm × 4.0 cm × 0.005 cm) were collected. The samples were provided by Good Fellow, U.K. Removal of organic contaminants from the surface of the specimens was done by rinsing in methanol for 15 min before the treatment. The samples were then cleaned in distilled water for 15 minutes in an ultrasonic bath and then dried at room temperature. All plasma treatments were carried out for 1 minute at atmospheric pressure and ambient temperature. The contact angle at 0.8 cm, 1.6 cm, and 2.4 cm from the center point of the polymer sample was measured. The contact angle measurement was done at four different locations on the same samples, and the average value of the contact angle was taken by the Rame-Hart contact angle goniometer (model 200).

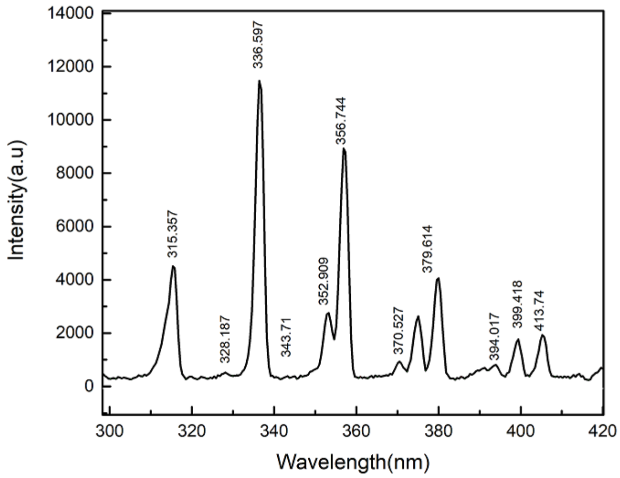

Figure 4: Spectra of the discharge at frequency 50 Hz and an applied voltage of 13 kV at atmospheric condition.

3. Results and discussion

3.1. Electrical characterization

The current density method is used to calculate the electron density [11,12].

Fig. 3 shows the current and voltage waveform of the discharge as a function of time. The electron density is calculated using the formula:

$$n_e = \frac{J_{av}}{e\,\mu_e E} \tag{1}$$

Where, J_{av} represents the average current density, e is the electronic charge and E is the electric field in the discharge region. The electron mobility μ_e at 13 kV for a Gaussian-shaped DBD is estimated to be 371.76 cm^2/V s using BOLSIG+ solver. Using these values in eq. (1), the electron density (n_e) is estimated to be 3.4×10^9 cm^{-3}.

3.2. Optical characterization

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

In this method, four suitable lines (two for N II lines and two for N III lines) were chosen from spectral lines of nitrogen obtained from the discharge. The optical characterization is carried out using the line intensity ratio method [13].

$$\frac{R_1}{R_2} = \frac{I_1/I_2}{I_3/I_4} = \left(\frac{A_{pq}}{A_{rs}}\right)\left(\frac{g_p}{g_r}\right)\left(\frac{\lambda_{rs}}{\lambda_{pq}}\right)\left(\frac{A_{uv}}{A_{xy}}\right) \left(\frac{g_u}{g_x}\right)\left(\frac{\lambda_{xy}}{\lambda_{uv}}\right)\exp\left[-\frac{E_p - E_r - E_x - E_v}{K_B T_e}\right] \tag{2}$$

In eq. (2), R is the ratio of the intensity of two lines, I is the intensity of the spectral line, A_{ji} is the transition probability of the transition $i \to j$, 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_B is 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_{ji}, g_i and E_i are obtained from the National Institute of Standards and Technology (NIST) Atomic Spectra Database [14]. The ratios of spectral lines (R_1/R_2) for various electron temperatures (T_e) are presented in Table 1.

Fig. 5 shows the plot of the ratio of the spectral lines for different electron temperatures. From our observation, the ratio of the

Table 1: Ratios of spectral lines for different electron temperatures.

Electron Temperature (T_e)	Ratio of the spectral lines (R_1/R_2)
0.5	11.6
0.6	6.13
0.7	3.88
0.8	2.75
0.9	2.11
1.0	1.71
1.1	1.43
1.2	1.23
1.3	1.09
1.4	0.98
1.5	0.89
1.6	0.83
1.7	0.77
1.8	0.72
1.9	0.68
2.0	0.65

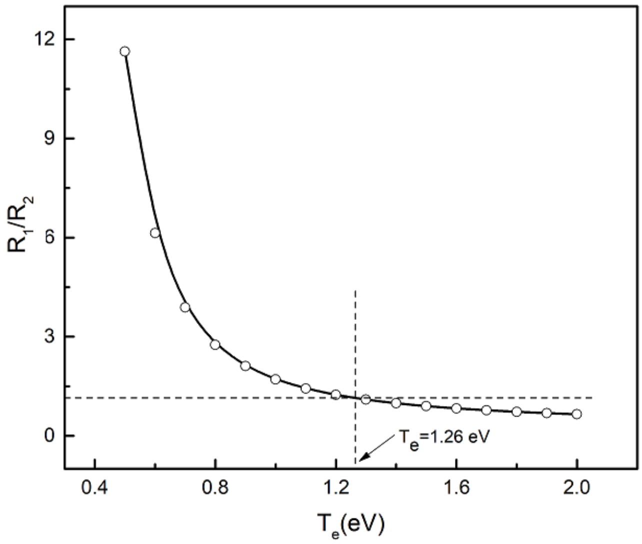

Figure 5: Plot of R_1/R_2 as a function of T_e.

intensity for the lines of NII and NIII was found to be 1.13. Using the values as obtained from the NIST database in equation (2), the electron temperature (T_e) was estimated to be 1.26 eV.

3.3. Contact angle measurements

For an ideal, smooth and homogeneous surface, the water contact angle is measured at equilibrium according to Young's equation [15].

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \tag{3}$$

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

The image of variation of contact angle of water by distance from the center of treatment after treating with plasma for PET polymer

Figure 6: Image of water drop contact angle on PET polymer.

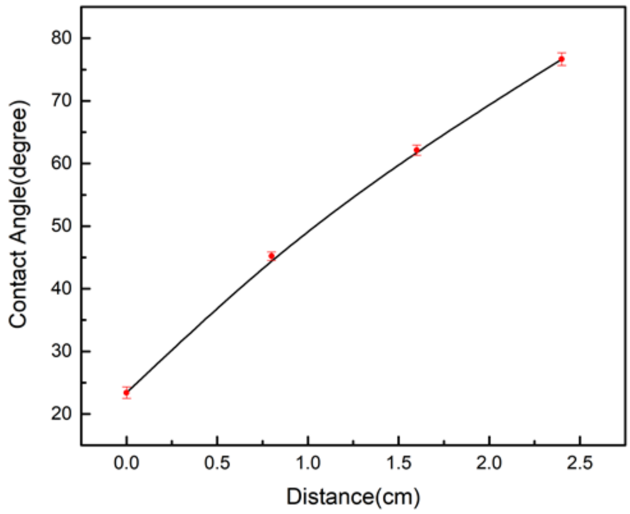

Figure 7: Variation of water drop contact angle as a function of distance for PET polymer.

is shown in Fig. 6.

Fig. 7 shows the variation of the water contact angle on the surface of the PET polymer on the basis of distance from the center of treatment. Initially, the contact angle of the PET sample was $82°$. It is seen that at 1 minute of treatment time, there is decrement in contact angle for the lowest value in the center of the polymer, i.e., $23.40°$, which shows a strong increase in wettability in the center of the PET polymer surface. The static water contact angle of the sample keeps increasing with an increase in distance from the center [16]. In this case, the distance between two consecutive points is 0.8 cm. The contact angle at 0.8 cm, 1.6 cm, and 2.4 cm from the center point is found to be $45.20°$, $62.13°$, and $76.67°$ respectively. The decrease in the contact angle may be due to the incorporation of polar species such as carbonyl (C=O), hydroxyl (-OH) and carboxyl (-COOH) groups on the treated PET surface [6,17–20].

4. Conclusion

Modification of PET was done using DBD at atmospheric pressure conditions. At atmospheric pressure, as seen from the electrical signal, the nature of the discharge is filamentary. The electron density and temperature of the discharge were found to be 3.4×10^{9} cm^{-3} and 1.26 eV, respectively. The result showed that the variation of contact angle within the polymer can also be studied by using a Gaussian shaped electrode. Also, it can be concluded that the variation of contact angles within the polymer depends on the electric field distribution by a particular electrode. Further, it is seen that the wettability of the polymer sample increases at the center, indicating an increase in hydrophilic nature. On the other hand, on moving from the center, the contact angle is found to increase. This change in the contact angle as a function of distance in the polymer might be due to the use of gaussian-planar shape electrodes.

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