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Surface modification of polyamide by 50 Hz dielectric barrier discharge (DBD) produced in air at atmospheric pressure

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ABSTRACT
Industrial applications of the dielectric barrier discharge (DBD) have a long tradition. However, lack of understanding in some of its fundamental issues, such as the stochastic behaviors, is still a challenge for DBD researchers. The work was carried out at line frequency, 15 kV and at atmospheric pressure. This work focuses on the study of the electrical and optical characteristics of DBD at atmospheric pressure to determine a suitable condition for utilization of the device for surface modification of polyamides (PA) (Nylon 6/6). In this work, films were treated by dielectric barrier discharge and the effects on the morphology and chemistry of the material was studied. Surface characteristics were examined via contact angle measurements and SEM. The wettability tests revealed the improvement of the hydrophilic character of the surface of polyamide films as the water contact angle measured after the plasma treatments significantly decreased. The corresponding changes of the total surface energy revealed a significant increase in its polar component. The improvement of the wettability of PA strongly depends on the treatment time. The outcomes of the experiments proved that the modification of surface properties via plasma treatment reach to its saturation point after certain treatment time thus reducing the necessity of further treatment.

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1. Introduction

Discharge characterization of dielectric barrier discharge (DBD) are often done using both numerical and experimental methods [1,2]. The scientific method includes techniques like optical and electrical means. The high electron temperature in nonthermal plasma causes changes on the surface properties of treated sample while its bulk properties remaining unaffected because of the low

ion temperature [3,4]. Most of the polymers treated industrially are heat sensitive, so treating them with hot plasma doesn't yield good results [5]. Here we discuss about the characterization of DBD and its application on the surface modification of polyamide at gas pressure condition.

The surface modification of polymer includes change in wettability and adhesion as well as the enhancement or reduction of friction on the polymer surface [6]. The surface energy of the polymer can be either increased or decreased according to the need of the experiment and the functional groups can be either added or wiped out from the surface. Surface energy is a very important property for applications of polymers. The low surface energy of polyamide causes that its adhesive properties are insufficient for bonding and printing. The poor adhesion of Polyamide to more polar polymers and other substrates represents a controversy, which might be solved with modification of the polymer [7]. For this reason, the securing of fine adhesion of printing inks or adhesives to PA surface necessitates to boost its surface energy by a convenient method of modification. So, industrial plasma treatment involves continuous and rapid treatment of huge quantity of polymeric sample every day. Reduction of treatment time of such polymeric samples by a few milliseconds can finally result out to the reduction of the treatment of thousands of samples by few minutes. So, determining optimal treatment time of the polymers sample is therefore, very important for industries which is the primary objective of the research.

2. Materials and Method

The experimental setup of the research is as shown as in Fig. 1. A cylindrical polycarbonate tube is used as the plasma chamber. The PC chamber is preferred due to its transparent nature allowing the experimentalist to see what actually is happening inside the discharge chamber. Two circular brass electrodes, each diameter 5 cm and thickness 1 cm are 3.5 mm apart and a polycarbonate sheet of thickness 2mm is used as dielectric. The working voltage for the entire experiment is set to be 15000 V. Current and voltage waveform are obtained using the digital oscilloscope (Tektronix TDS2000). A high voltage probe (PINTEK HVP-28HF) is used for the determination of voltage across the electrodes. Similarly, Optical characterization of DBD at both the conditions is carried using ocean optics (USB2000+). The samples of polyamides (Nylon 6/6) are cut into (3 cm × 1.5 cm) rectangular pieces. They are then washed by isopropanol and put into an ultrasonic bath for further cleaning. Samples are placed on the polycarbonate sheet between the electrodes. Thus, treated sample are taken for surface characterization. Contact angle was measured using a contact angle goniometer (Rame-Hart Model 200). In this work, LEO (500) /Zeiss Field-emission scanning electron microscope (SEM) was used to examine surface morphology.

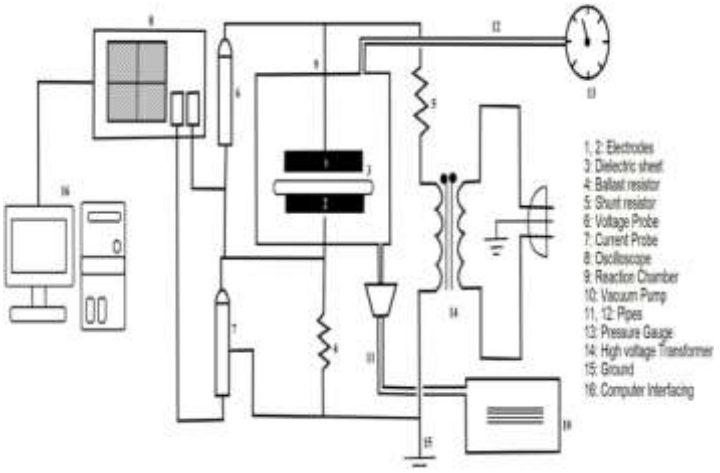

Fig. 1: Schematic diagram of the experimental Setup.

3. Results and Discussion

Electrical characterization

The value of electron density (n_e) has been calculated by using Power Balance Method [8,9].

This method is based upon the principle that the energy lost by the plasma parameters is equal to the power delivered by the source. The balance between the input power from high voltage power supply (P) and power lost in the plasma leads to.

$$n_e = \frac{P_{ab}}{2Av_bE_{lost}} \text{.....(1)}$$

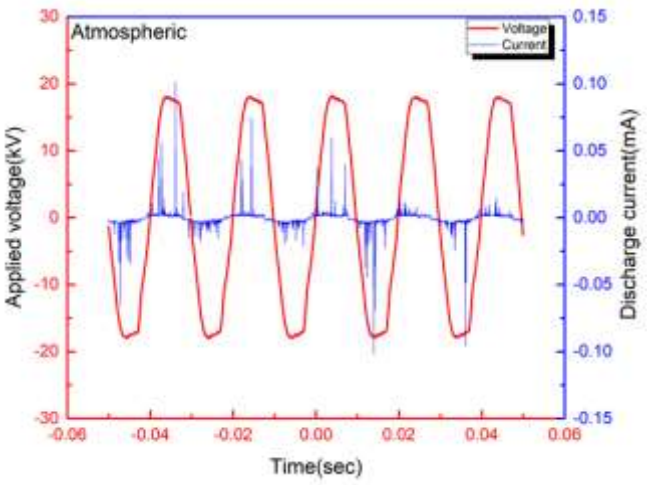

Fig. 2: Electrical characterization of DBD at atmospheric condition.

Fig.2 shows the current and voltage waveform as a function of time of the dielectric barrier discharge generated using line frequency. The calculation was made by using the values given below:

Applied voltage $= 15000\,V$, Discharge current = $0.0386\,mA$, Inter- Electrode separation $= 3.5\,mm$, Applied frequency $= 50\,Hz$, Area of each electrode $= 20.43\,cm^2$, Bohm velocity $(v_b) = 2 \times 10^5\,cm/s$, $E_{lost} = 50\,eV$ (in our condition) and P_{ab} is the total power absorbed by the capacitively coupled plasma. Using these values, the electron density (n_e) was found to be $2.52 \times 10^{13} cm^{-3}$ at atmospheric condition.

Optical characterization

For optical characterization of DBD, a small hole is made on the cylindrical polycarbonate tube and, an optical fiber is inserted there. The discharge of the DBD is made to pass through the optical fibre and the spectra is recorded by the Ocean Optics (USB2000+) at atmospheric conditions. Fig. 3 shows the spectra of the discharge and their corresponding intensities, and wavelength at an atmospheric pressure condition.

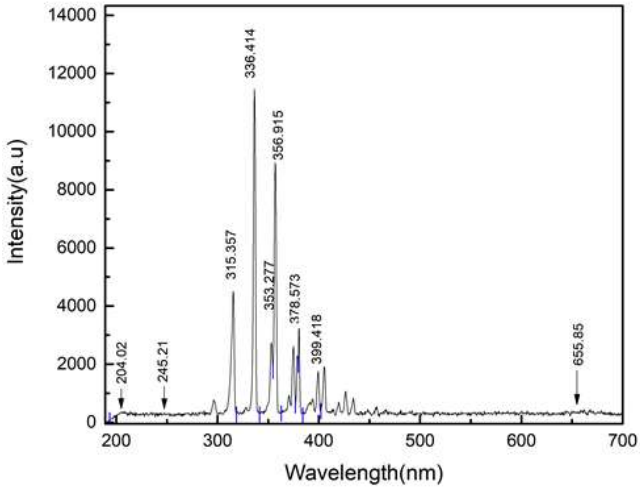

Fig. 3: Spectra of the discharge at atmospheric pressure.

In this method four suitable lines; two for NII (204.02 nm, 655.85 nm) and two for N III (245.21nm, 378.57 nm) were chosen from spectral lines of nitrogen obtained from the discharge. The optical characterization is carried out using line intensity ratio method [10,11].

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

Here, in equation (2), 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 $i \longrightarrow j$, 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_{ij}, g_i and E_i are obtained

from the National Institute of Standards and Technology (NIST) Atomic Spectra Database [12]. **Table 1:** shows the values of transition probability (A_{ji}), statistical weight of upper level (g_i) and energy of the upper level (E_i) for NII and NIII lines obtained from NIST database.

Nitrogen Lines (λ)	**Transition probability (A_{ji}) (S^{-1})**	**Statistical weight of upper level (g_i)**	**Energy of upper level (E_i) (eV)**
NII (204.02nm)	2.11×10^{7}	5	21.62
NII (655.85nm)	1.43×10^{6}	5	41.73
NIII (245.21nm)	1.21×10^{7}	6	23.26
NIII (378.57nm)	2.40×10^{6}	5	40.59

Using the above data in equation (3.6) mentioned above, we obtain,

$$\frac{R_1}{R_2} = 0.506exp\left[\frac{2.78}{K_B T_e}\right]$$

Taking $T_e = 0.5\ eV$, corresponding intensity ratio $\frac{R_1}{R_2} = 131.4$. Similarly, the other values of T_e and their corresponding intensity ratio $\frac{R_1}{R_2}$ are listed in Table 2.

Table 2: Value of $\frac{R_1}{R_2}$ for different T_e.

Electron Temperature (eV)	**Intensity Ratio $\frac{R_1}{R_2}$**
0.5	131.47
0.6	52.04
0.7	26.84
0.8	16.34
0.9	11.10
1	8.15
1.1	6.33
1.2	5.13
1.3	4.29
1.4	3.68
1.5	3.22
1.6	2.87
1.7	2.59
1.8	2.37

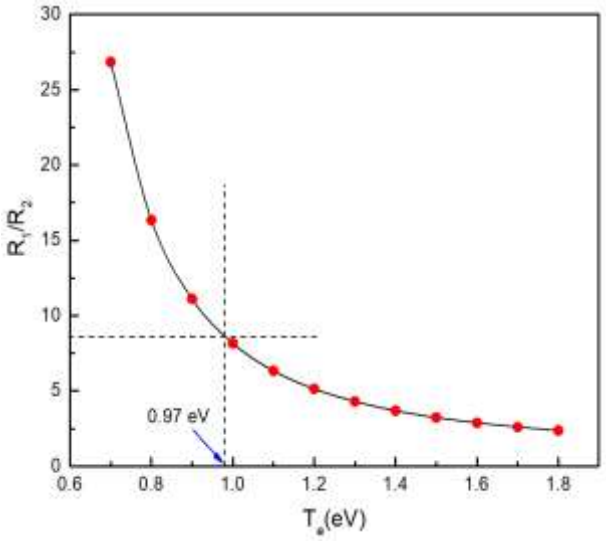

Fig. 4: Optical characterization of DBD at atmospheric condition.

Fig.4 is the graph plotted between electron temperature T_e and corresponding intensity ratio $\frac{R_1}{R_2}$. This graph is used to determine the electron temperature using the value of $\frac{R_1}{R_2}$ obtained from the intensity ratio. From the OES spectra, the value of the ratio of the intensity of spectral lines is found to be 8.58 which corresponds to the electron temperature of 0.97 eV.

Contact angle and surface free energy measurements

The static contact angle measurements are made before the treatment and immediately after the treatment by dropping 4 μl of distilled water (H_2O) and glycerol ($C_3H_8O_3$) on the surface of the PA samples. For smooth and homogeneous surface, the water contact angle and surface free energy is measured at the equilibrium according to the Young's equation, and Owens Wendt Kaeble methods respectively [13,14].

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} .....(3)$$

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.

For two liquids i and j,

$$\gamma_{li}(1+\cos\theta_i) = 2\left(\gamma_{li}^d \gamma_s^d\right)^{\frac{1}{2}} + 2\left(\gamma_{li}^p \gamma_s^p\right)^{\frac{1}{2}} .....(4)$$

$$\gamma_{lj}(1+\cos\theta_j) = 2\left(\gamma_{lj}^d \gamma_s^d\right)^{\frac{1}{2}} + 2\left(\gamma_{lj}^p \gamma_s^p\right)^{\frac{1}{2}} .....(5)$$

Surface free energy (γ) was calculated in terms of polar γ_s^p and dispersive γ_s^d components. The addition of these two components eventually gives the total surface free energy of the solid.

Fig. [5, 6] show the variation of water contact angle and surface free energy of PA surface as the function of treatment time. The contact angle is found to decrease with the increase in treatment time. After few minutes it finally saturates. Treatment of PA by atmospheric pressure dielectric barrier discharge is able to change its contact angle from 57.51^0 (control) to a minimum value of 29.01^0 after 30 seconds. When the treatment time exceeds 30 seconds, the measured water contact angle nearly seems to reach a saturation state suggesting that the physical and chemical changes induced

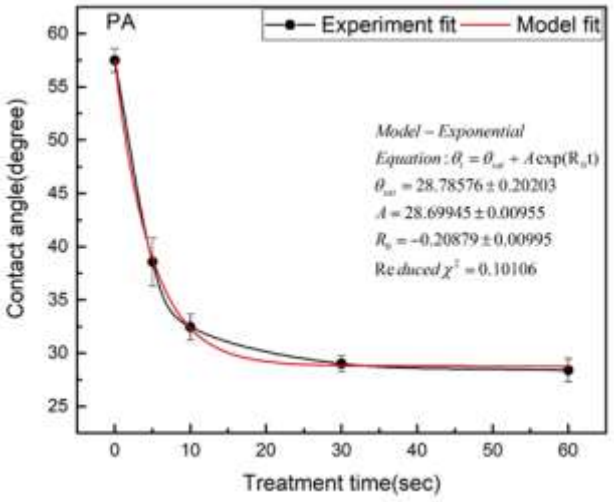

Fig. 5: Contact angle measurement at atmospheric pressure.

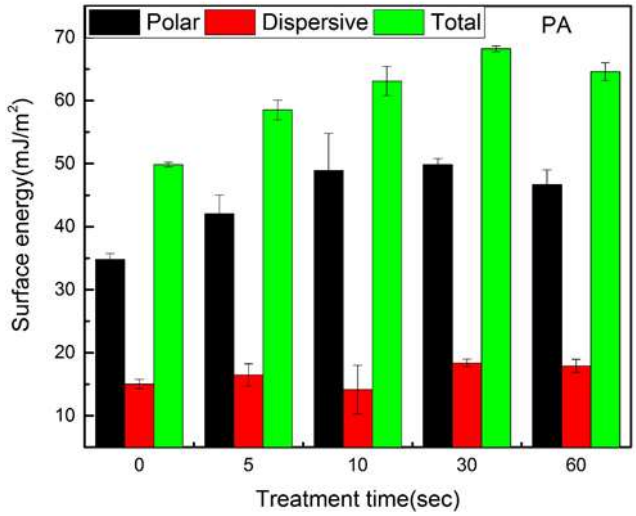

Fig. 6: Surface energy measurement of Polyamide at atmospheric pressure.

by the plasma is also in saturation state [15]. Also, the treatment of PA by atmospheric plasma is able to change its surface energy from 49.84 mJ/m^2 (control) to about 64.91 mJ/ m^2. Similar trend is also observed for the polar component and it is mainly due to the incorporation of the polar species such as carbonyl (C=O) and carboxyl (-COOH) groups on the treated PA surface. The dispersive

component does not have any contribution to increase the wettability of the PA surface [16]. It is found that the further treatment of PA also does not cause any significant changes in the surface free energy reducing the requirement of further treatment.

SEM analysis

Fig. [7-8] show the SEM micrographs of control and plasma treated PA films at atmospheric pressure. As can be seen in the micrograph, the untreated polymer surfaces is characterized by organized lamellae. This texture of the untreated sample of the polymer pertains to the process of the polymer film production (which is possibly induced by the film blow procedure during production) and not due to plasma treatment. It can be seen that the surfaces of the air plasma treated polymer is changed with slightly increased non-uniform roughness compared to the untreated polymers. The gradual increase in the particle grain size with the image scan area can be attributed to the etching of the polymer surface by plasma treatment [17].

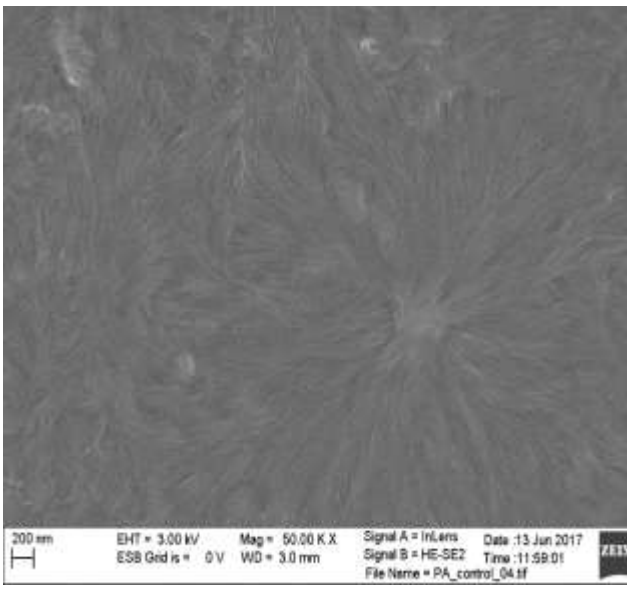

Fig. 7: SEM micrograph of control sample of Polyamide.

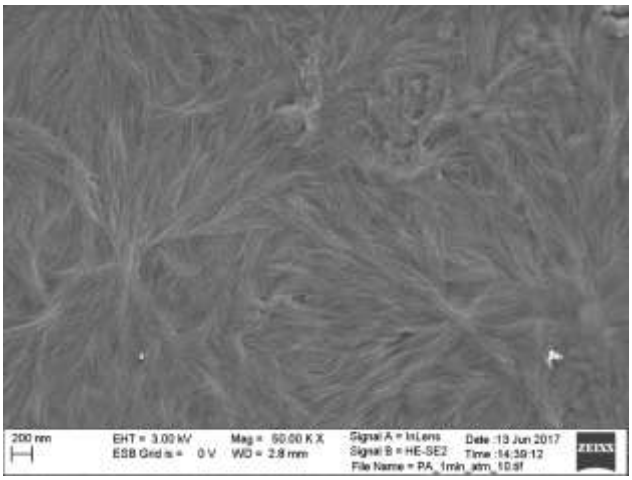

Fig. 8: SEM micrograph of plasma treated sample of Polyamide at 1 minute.

4. Conclusions

The results of this research showed that a relatively homogeneous discharge can be achieved at an atmospheric pressure condition. Treatment of PA using dielectric barrier resulted in improvement on hydrophilicity of the polymeric material. The improvement of wettability of PA strongly depends on the treatment time. During the experiment, contact angle of polymers after plasma treatment was found to decrease effectively whereas, corresponding surface free energy was increased. SEM micrographs of the plasma treated PA samples revealed the change in the surface morphology of the film. It was also seen that the change in surface properties of the treated sample reached its saturation point, eliminating the requirement of further treatment. So, the polymer industries can therefore save the energy by calculating the optimal treatment time for the sample over which there is noticeable change on the surface properties.

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