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Experimental Study of an Atmospheric Pressure Dielectric Barrier Discharge and PET Surface Modification

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ABSTRACT
A homogeneous dielectric barrier discharge (DBD) in argon was produced by applying high voltage A.C. source of potential difference (0-20) kV operating at a frequency of 10-30 kHz across two parallel plate electrodes with glass as dielectric barrier. The discharge was characterized by optical emission spectroscopy (OES) and electrical measurement. Four argon emission lines from the discharge were analyzed and the electron temperature was estimated by line intensity ratio method. The electron density in the discharge was estimated by power balance method. An investigation of the effect of inter-electrode distance on the electron density was made. The results showed that the electron temperature is less than 1 eV and the electron density is of the order of $10^{11}cm^{-3}$ which varied with the inter electrode distance. Discharge was applied for surface modification of polyethylene terepthalate (PET). Modified surfaces were studied by contact angle measurement and FTIR spectroscopy.

Key words: Electron temperature, electron density, DBD, optical emission spectroscopy, power balance.

I. Introduction

Atmospheric pressure dielectric barrier discharges (DBDs) are non thermal and non equilibrium plasmas [1]. Atmospheric pressure non equilibrium plasmas have been widely studied for several emerging applications such as surface and material processing biological and chemical decontamination of media, light source, absorption and reflection of electromagnetic radiation and synthesis of nanomaterials [2]. This process can be improved by a better understanding of basic plasma phenomena and by knowing its properties. The plasma properties depend on several parameters, such as, the electrode geometry, cooling system, excitation frequency, power injected, gas composition and type of dielectric barrier [3].

The electron density and electron temperature are the most fundamental parameter in gas discharges and play a very important role in understanding the discharge physics and optimization of the operation of plasma [3, 4]. Different methods are employed to measure the electron density and electron temperature in plasma. In atmospheric-pressure discharge system, both the probe and the microwave-based methods are difficult to use due to the small plasma dimension and strong collision process. The OES based technique is suitable for measurement of electron density and electron temperature. To measure the electron temperature line intensity ratio method is used, in which the intensity ratio of emission lines is related to electron temperature and electron density.

OES has been used for the measurement of electron temperature and electron density in different types of plasmas [5, 6, 7, 8]. Low temperature plasmas are widely applied for the surface treatment of polymers because of their several advantages over other conventional methods. Jie-Rong, *et al* reported wettability of Poly(ethylene Terephthalate) film treated with low-temperature plasma and their surface analysis by ESCA[9]. Novák *et al* also studied the surface propertis of poly(ethylene terephthalate) treated by low-temperature plasma [10]. The present experiment uses a power supply working at 27 kHz to produce the discharge at atmospheric pressure. The discharge is found to spread homogeneously over the whole area of the electrode and known as the atmospheric pressure glow discharge (APGD).

In this paper, electron temperature in atmospheric pressure DBD in air/argon environment is measured by line intensity ratio method and electron density is determined by power balance method. The relationship between the surface wettability and the surface structure of PET is investigated by FTIR spectroscopy. The change in hydrophilic property of the sample has been studied.

II. Experimental

The experimental arrangement is shown in Fig.1. The electrodes are made up of two brass discs, 7mm thick and 51mm in diameter. A glass plate of thickness 1.2mm was used as dielectric barrier between the electrodes. A high voltage AC source (0-

20) kV and frequency (10-30) kHz was applied to electrodes through a current limiting resister of 10kΩ.

The whole apparatus is enclosed in a cylindrical chamber and argon is passed into it at a flow rate of 2l/m. The applied voltage and current were measured by high voltage probe (Tektronics TDS2000). The experiment were conducted with inter electrode spacing varying between 1-3mm

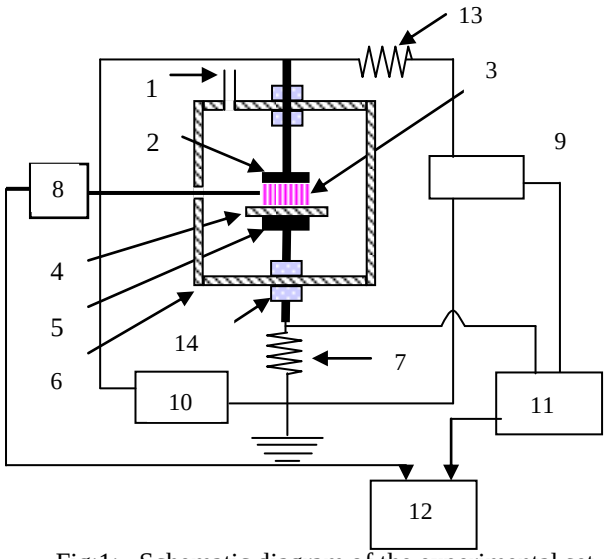

Fig:1: Schematic diagram of the experimental set-up.
1-Gas inlet, 2- power electrode, 3-Discharge, 4-Glass plate , 5-Grounded electrode, 6- Plasma reactor, 7- Resistance 10 kΩ, 8- Linear Array Spectrometer VS140, 9- Voltage probe, 10- Power supply (A.C), 11-Osciloscope , 12-Computer, 13-Resistance 10 MΩ , 14- Teflon screw.

Optical emission spectra were recorded by liner array optical spectrometer (Lynear VS140). Contact angles were measured by rame hart goniometer. The ATR-FTIR spectroscopy measurements of PET foils were performed with IR Prestige-21, shimadzu, Japan having a resolution of 4 cm^{-1}, a scan range was 4000 – 400 cm^{-1}, and a total of 50 scans per analysis.

III. Result and Discussion

3.1 Measurement of Electron Temperature by Line Intensity Ratio Method:

Fig: 2 shows the OES of the discharge in the range of 250nm-850nm. The applied voltage, discharge current and spectrum are simultaneously measured and analyzed for determination of electron temperature. Using line intensity method, four suitable lines (two for ArI and two for ArII are chosen and electron temperatures is estimated using the lines intensity ratio method. For the measurement of electron temperature, equation (1) is used [5,6,7].

$$\frac{R_1}{R_2}=\frac{I_1/I_2}{I_3/I_4}=\left(\frac{A_{pq}}{A_{rs}}\right)\left(\frac{g_p}{g_r}\right)\left(\frac{\lambda_{rs}}{\lambda_{pq}}\right)\left(\frac{A_{uv}}{A_{xy}}\right)\left(\frac{g_u}{g_x}\right)\left(\frac{\lambda_{xy}}{\lambda_{uv}}\right)\exp\left[-\frac{E_p-E_r-E_x+E_u}{kT_e}\right]\text{.....(1)}$$

Where R is the ratio of intensity of two lines, I is the intensity of spectral lines, A_{ij} is the transition probability of the transition i→j, g_i - The statistical weight of the upper level, λ - wave length of the radiation, E_i - energy of the upper level, K - Boltzmann constant and T_e - electron temperature Considering two Ar I lines of wavelength 696.54 nm, and 751.034 nm and two Ar II lines with wavelength 314.13 nm and 378.75 nm and plot of R_1/R_2 against T_e has been made, the electron temperature has been found to be 0.89eV. This result is in good agreement with the results reported in previous work.

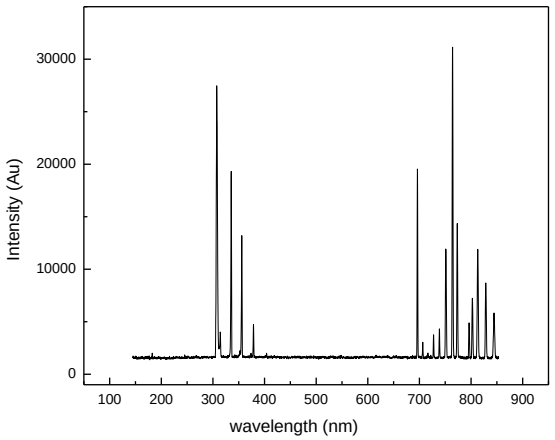

Fig. 2 Optical emission lines of atmospheric pressure discharge produced in Argon.

Electron temperature thus determined is used to calculate the electron density by using the Eq. (2) given below

$$n_e=2\left(\frac{I_1}{I_2}\right)\left(\frac{\lambda_1}{\lambda_2}\right)\left(\frac{A_2}{A_1}\right)\left(\frac{g_2}{g_1}\right)\left[\frac{2\pi m_e kT_e}{h^2}\right]^{\frac{3}{2}}Exp[-\frac{E_1-E_2+E_i}{KT_e}]\text{--(2)}$$

The use of Eq. (2) is made for calculation of n_e from different lines and average values of n_e= 3.47032×10^{11} cm^{-3} is obtained.

3.2 Determination of Electron Density by Power Balance Method

The glow mode discharge is homogeneously spread over the whole electrode area, so the plasma density can be estimated from a power balance method. In this method electron density is given by [7].

$$n_e=\frac{p}{2Aev_bE_{lost}}\text{----(3)}$$

Where A - Area of each electrode=20.43cm^2, v_b - Bohm velocity = 2×10^5 cms^{-1}, E_{lost} = 50eV (in our

condition), Applied frequency = 27 kHz, Gas flow rate 2l/min, Dielectric = 1.5mm thick glass.

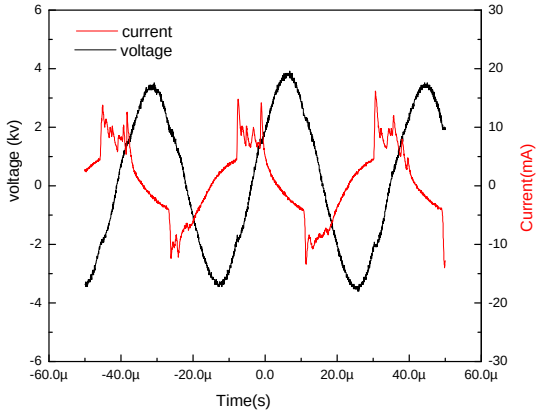

Fig.3: Voltage and current waveforms of discharge.

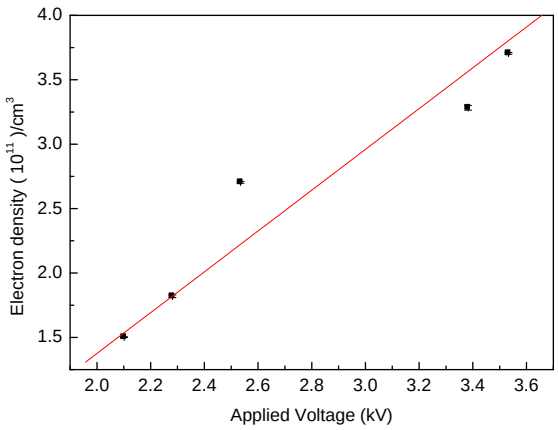

Fig 4: Electron density as a function of applied voltage.

By using Eq. (3) electron density was calculated for different value of applied voltage and the variation of electron density with applied voltage is shown in Fig 4. It is evident that electron density increases linearly with the applied voltage.

3.3 Measurement of Contact Angle and Surface Energy

Contact angles were measured on PET surface treated with APPJ in argon for exposure time 0–60 seconds. The measurements of the contact angles were performed by contact goniometer using distilled water and glycerol on different positions of the treated sample. Surface energy was calculated using the Owens-Wendt Kaelble method. In this method, it is possible to determine the solid surface energy (γ) as the sum of polar (γ^p) and dispersive (γ^d) contribution using at least two different test liquids (water and glycerin) [9, 10, 11,12]

$$\gamma_l(1+\cos\theta) = 2\left[\gamma_l^d \gamma_s^d\right]^{\frac{1}{2}} + 2\left[\gamma_l^p \gamma_s^p\right]^{\frac{1}{2}} \text{----(4)}$$

The dependence of contact angle and surface energy on exposure time for PET is shown in Fig: (5 and 6). The images of water drops on the surface of untreated and plasma treated PET sample are shown in the inset of Fig 5. The value of contact angle decreases and consequently the surface energy increases with the treatment time. The increase in surface free energy is attributed to the functionalization of the polymer surface with hydrophilic groups.

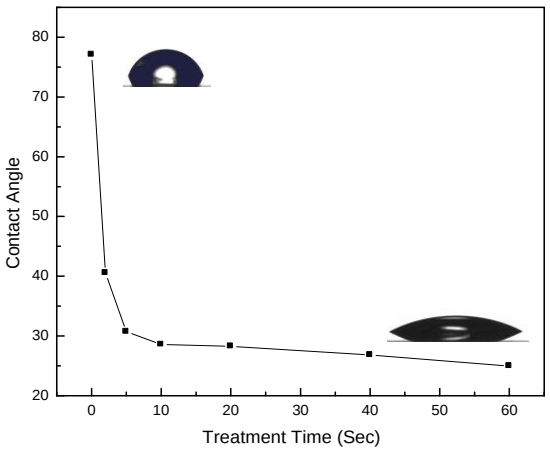

Fig 5: Water contact angle on PET as function of treatment time in Argon plasma

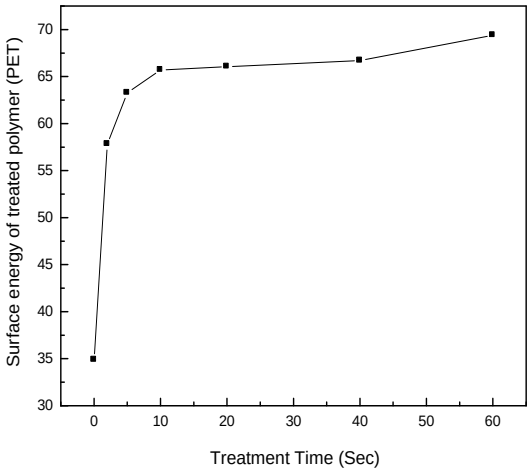

Fig 6: Surface energy of PET as function of treatment time in Argon plasma

3.4 Surface Analysis of PET

The wettability of the sample is related to the presence of a particular functional group that resides on the outermost surface layer. The relationship

between the surface chemical structure and surface wettability of plasma treated PET was characterized by Fourier Transform Infrared (FTIR) Spectroscopy.

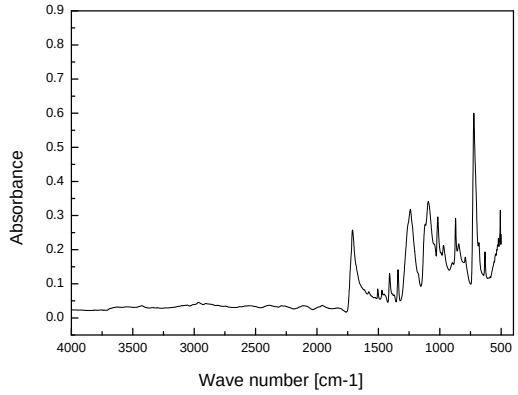

Fig.7 Furrier Transform infrared (FTIR) Spectroscopy control sample

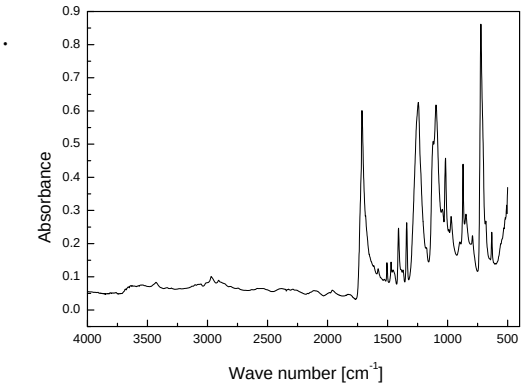

Fig.8 Furrier Transform Infrared (FTIR) Spectroscopy of plasma treated PET

The chemical changes in surface properties of plasma-treated polymer are analyzed using ATR-FTIR spectroscopy. Fig.7 shows the ATR-FTIR spectra of unmodified PET. FTIR spectra for PET treated in atmospheric pressure plasma in Ar gas is shown in Fig 8 for comparison.

It is also observed from the FTIR spectra (Fig. 7and 8) that there is a change in intensity of absorption peaks corresponding to certain functional groups. The wave number region: from 3600 to 2500 cm^{-1}, where the C–H and O–H stretching vibrations of different types of H-bonds occur.

Spectrum of PET has the characteristic absorption peaks at 1714 cm^{-1} (C=O bonds), 1410, 1018, and 872 cm^{-1} (vibration of aromatic ring), 1340 and 1177 cm^{-1} (bending vibration of $-CH_2$ groups), 1244 and 964 cm^{-1} (stretching vibration of C-O bonds), 690 cm^{-1} and 750 cm^{-1} phenyl group (=C-H & C=C) 1124 and 1100 cm^{-1} (stretching vibration of C-O bonds due to amorphous and crystalline structure of PET respectively) [12,13,14].

For PET treated in APPJ, the broadening of the C=O stretch at 1714 cm^{-1} has appeared due to creation of oxygen-containing sites .

The information from the FTIR spectra indicates that the carbon content decreases and the oxygen content increases in the surface of PET, and a large amount of oxygen polar functional groups are introduced into the surface of plasma-treated PET. This is responsible for improving the wettability of PET.

IV. Conclusion

Atmospheric pressure argon plasma has been produced and characterized by optical and electrical methods. Electron density (n_e) and Electron temperature (T_e) were found to be $3.36\times10^{11}cm^{-3}$ and 0.786eV respectively with the electrode gap of 2mm. Electron density and electron temperature were found to be dependent on the applied voltage for constant inter electrode distance.

Atmospheric pressure argon plasma treatment of PET surface resulted an improvement on hydrophilicity. It is mainly due to the increase in the polar component of the surface free energy after plasma treatment which indicates the formation of polar functional groups on the surface. The improvement of wettability of PET strongly depends on the treatment time. This system can be very useful for the treatment of thermally sensitive materials and also for the treatment of biological samples.

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