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Experimental Study of Atmospheric Pressure Argon Plasma Jet and Surface Treatment of Polyethylene Terephthalate

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Abstract: *Atmospheric pressure plasma jets (APPJ) have been established as suitable sources of low-temperature and non-equilibrium plasmas. In this paper, an atmospheric pressure plasma jet sustained in argon gas has been used to modify the surface properties of the Polyethylene terephthalate (PET) samples. The surface properties of the untreated and plasma treated PET samples were characterized by using a ramhart contact angle goniometer. Two different test liquids distilled water and glycerol was used and the surface energy of the PET samples was determined by Owen-Wendt-Kadble method. Results showed that the water contact angle on PET reduces from 77° for control sample to 25° after 60s of plasma jet exposure. Chemical modifications of the PET surfaces were investigated with Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) Spectroscopy. FTIR analysis of the plasma-treated PET films showed that plasma treatment introduces hydrophilic functional groups on polymer surface. Thus APPJ in argon can effectively modify the surface property of the polymers leading to enhance hydrophilicity.*

Key words: *Plasma jet, contact angle, surface energy, ATR-FTIR*

I. Introduction

PET is a widely used material because of good mechanical and chemical properties but it has low surface energy. Their use in various applications involving composite and biomaterials, packing, printing, dying etc, has been restricted due to their poor wettability, dyeability and adhesion. A large number of techniques have been used to overcome this problem. These include the use of chemical treatments, flame, corona as well as treatment by both low pressure and atmospheric pressure plasmas [1,2]. Among various non-thermal plasma sources, the dielectric barrier discharges (DBDs) are studied mostly for surface modification of polymers because of easy formation of stable plasma and their scalability. Numerous studies show that the highly reactive species in the discharge regime of DBD can interact with the surface of materials and can induce changes in surface properties [3-5]. However, atmosphere pressureDBD usually operates in the narrow gap (usually several millimeters) between two parallel-plate electrode, which limits the size and shape of the object to be treated. Recently, a novel atmospheric pressure plasma jet (APPJ) devices have attracted significant attention. Working under gas flow conditions, the active species can be blown out of the APPJ reactor to form a luminous plasma jet with moderate energy density in open air, thus fascinating its applications in material surface treatment, biomedicine, and thin-film deposition. It has no limitations on the sizes of the objects to be treated, thus can also be used to modify even 3-D structures [6-8]. The APPJ devices operated in different gases are developed and used for surface modification of some polymer materials [9-14].

The process of modification of polymer surface can be improved by a better understanding of basic plasma phenomena and by knowing key plasma parameters. The electron density, electron temperature, densities and temperature of different species (charged particle, reactive species, neutrals etc.) are the most fundamental parameters in gas discharges and play important role in understanding the discharge physics and optimization of the operation of plasma [15]. Different methods are employed to measurethe electron density and electron temperature in plasma. In atmospheric-pressure plasma jet system, both the probe and the microwave-based methods are difficult to use due to strong collision process. The OES (optical emission spectroscopy) based technique is suitable for measurement of electron density, electron temperature and various species (reactive oxygen species (ROS) such as singlet oxygen, hydroxyl radical and reactive nitrogen species (RNS)) present in the plasma [16]. To measure the electron temperature and electron density, line intensity ratio method is used, in which the intensity ratio of emission lines is related to electron temperature and electron density [17, 18]. For measurement of electron density power balance method is used. Electron density was measured by using power balance method [19].

In this paper, polyethylene terephthalate (PET) films are treated by APPJ in argon only and argon/oxygen plasma jet. The influences of different main operation parameters including discharge power density, treatment distance and treatment time on surface modification are explored in terms of hydrophilicity of PET surface.

II. Experimentals

Plasma jets concerned in this paper are generated in a glass capillary tube with an inner diameter of 3.0 mm and an outer diameter of 5 mm. The electrodes, 1.0 cm wide, are made of aluminum foil wrapping the capillary tube and the distance between the inner edges of two electrodes is 15 cm. The ground electrode is on the upstream side; the active electrode is on the downstream side and with its outer edge at about 0.5 cm from the tube orifice. Schematic diagram of the present experimental setup of the atmospheric-pressure plasma jet apparatus is shown in Fig.1. Argon and oxygen gases are used as the working gas; and the flow rate is controlled by a volume flow meter. The flow rate of the argon gas was restricted below 15 l/m so that the flow velocity would not exceed the limit for a laminar argon flow. We used a high frequency power supply at a frequency of 27 kHz and voltage in the range of 0-20 kV for the excitation and sustaining the discharges.

The optical emission spectrum (OES) was collected perpendicular to the jet using an Optical Spectrometer (Ocean Optics USB+2000 Spectrometer) having a spectral range of 200-1100 nm with a resolution of 2.2 nm full width at half-maximum (FWHM). The OES data were achieved by using a personal computer (PC) equipped with relevant software (Lynex) for both driving and acquisition. The absolute irradiance of the active species in the plasma was obtained. During the measurement of the optical emission spectra, the exposure time was 100 ms. Emission intensities of the active species were collected at different position of the plasma jet through an optical fiber with a diameter of 100 μm.

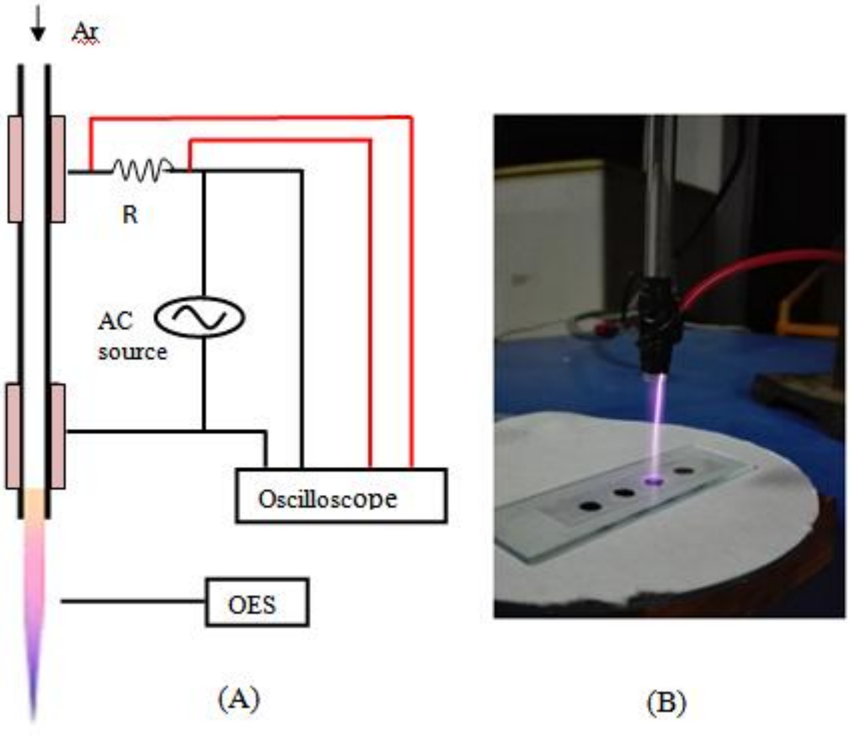

Fig.1: Schematic diagram of experimental setup for generation of atmospheric pressure argon plasma jet (A) and photograph of plasma jet in operation at K.U.Lab(B)

III. CHARACTERISATION OF PLASMAJET

Electrical Method

The voltage applied to the discharge was measured using a 10:1 voltage probe (Tektronix 2002TDS), and the discharge current was recorded using a current probe. Further, a digital oscilloscope (Tektronix TDS2002) was employed to acquire the voltage and current waveforms. The typical waveforms of discharge voltage and discharge current at fixed discharge voltage of 3.5 kV and a discharge frequency of 27 kHz are shown in Fig. 2. There is a positive current pulse and a negative current pulse per cycle of the applied voltage, which is a typical characteristic of atmospheric pressure glow- like discharges.

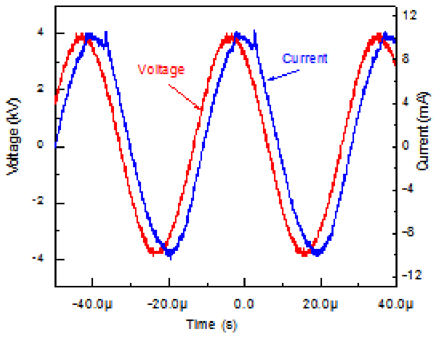

Fig.2 Typical current voltage wave form of APPJ

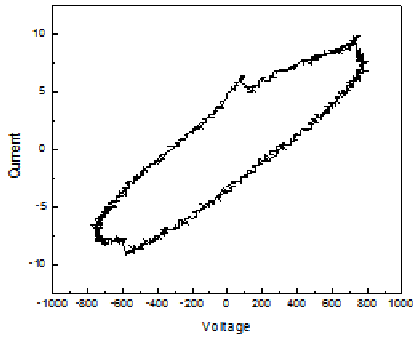

Fig.3 Lissajious figure of APPJ

The current - voltage figure was used to evaluate the power consumed in the discharges, i.e. area under the graph plotted between current vs voltage gives the power consumed by APPJ discharge which was shown in Fig. 3.

The estimation of electron density can be done by the power balance method, in which the total energy lost by the electron in the plasma is balanced by the input power. [16]

$$n_e = \frac{P_{ab}}{2Av_b E_{lost}} ----------(1)$$

Where P=VI is the input power during the discharge, A is the surface area of the electrode, e is the charge on the electron, v_b is the Bohm velocity. Electron density in the discharge was found to be 1.546×10^{16} cm^{-3}.

3.2 Optical Characterization of APPJ

The OES technique used for determination of plasma parameters is based on the measurement of relative intensities of two or four spectral lines of same atomic species. The intensity of spectral lines depends on KT_e and proportional to the population density of excited states. Hence KT_e can be determined by using well known Boltzmann plot [20].

$$KT_e = \frac{E_2 - E_1}{\log\left[\frac{I_1}{I_2}\frac{\lambda_1}{\lambda_2}\frac{g_2}{g_1}\frac{A_2}{A_1}\right]} ----------(2)$$

In Eq. (2), indices 1 and 2 refer to the first and second spectral lines. I - measured intensity of selected spectral lines, K - Boltzman constant, E- excited states energy, g- statistical weight, and A- transition probability.

The Boltzman plot method is valid if the discharge plasma under study is in complete local thormynamic equilibrium (LTE) [21]. But in our experiment it is difficult that LTE will hold due to low plasma density. Even though this method may not be used for the exact determination of KT_e and n_e; it can still provide us approximate values of plasma parameter under varying working condition of APPJ discharge. In the spectrum, the Argon lines are observed in the range of (180-1000) nm and KT_e are determined by selecting two Argon spectral lines. The intensity of these spectral lines is obtained from the observed spectrum given Fig.4 . The E, g and A for the selected lines are taken from the NIST Atomic spectra data sheet, using all these value in Eq. (2), the KT_e can easily be determined. The electron density n_e can be determined by using the relative intensity of atomic and ionic spectral lines in Boltzman-Saha equation [22].

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

I_1 - is the intensity of the Ar-I $\qquad$ I_2 - Intensity of Ar-II line

λ_1, λ_2 - Wavelengths $\qquad$ A_1, A_2 - Transition probabilities

g_1, g_2 - Statistical weights of level (neutral) and (ionized) respectively

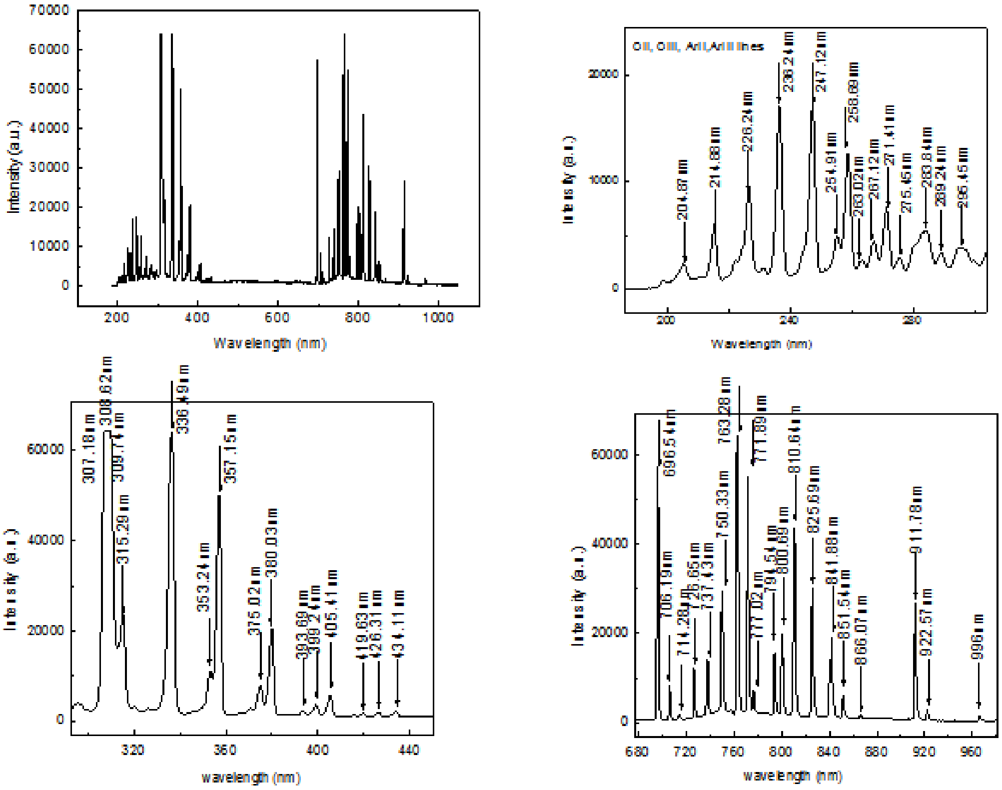

Fig.4. Optical emission lines of atmospheric pressure plasma jet in Argon at discharge frequency 27 kHz and applied voltage 3.5 kV

The use of Eq. (2) is made for calculation of T_e for different sets of spectral line and the average value of T_e is calculated to be 0.37eV. The use of Eq. (3) is made for calculation of n_e for different sets of lines and average values of $n_e=3.42\times10^{16}$ cm^{-3}.

IV. Measurement of Contact Angle and Surface Energy

Contact angles, immediately after plasma treatment, was measured on PET surface modified with APPJ exposure time of 0–60 seconds by goniometry with static water drop method. The Sessile Drop technique was used for the characterization. The measurements of the contact angle were performed using distilled water and glycerin on different positions of the treated PET. Surface energies were 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)[23].

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

The dependence of contact angle and surface energy on plasma exposure time for PET is shown in Fig: (5 and 6) by keeping rest of experimental conditions such as argon gas flow rate, sample-nozzle distance and the discharge voltage. The value of contact angle decreases as the time of treatment increases. But it was found that surface energy increases as treatment time increases. The increase in surface free energy is attributed to the functionalization of the polymer surface with hydrophilic groups.

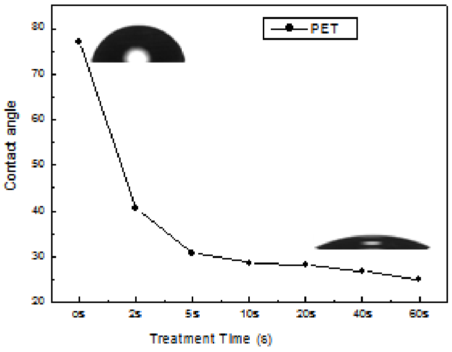

Fig.5. Water contact angle as function of treatment time

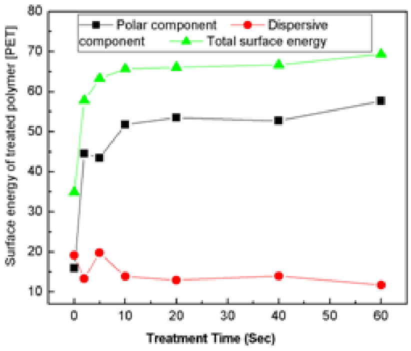

Fig.6. Surface energy of polymer as function of treatment time

For a fixed applied voltage, flow rate of argon and sample-electrode distance, the contact angle decreased exponentially with the treatment time. As a result of this, surface energy of the sample increased nearly to a saturation value as shown in Fig.6. The decrease in contact angle can be attributed to increase in surface roughness and incorporation of hydrophilic functional groups. This effect is obviously time dependent which is observed in the result. However, saturation in the value of surface energy is observed beyond 60s of treatment which may be due to the equilibrium between the formation of hydrophilic functional groups on the surface and their removal by etching.

V. Surface Analysis of PET

The wettability of the sample is tightly related to the presence of a particular functional group that resides in the outermost surface layer. The relationship between the surface chemical structure and surface wettability of plasma treated PET was characterized by Furrier Transform Infrared (FTIR) Spectroscopy.

The ATR-FTIR spectroscopy measurements of PET foils were performed with PerkinElmer Spectrum 100 FTIR spectrometer fitted with Universal Attenuated Total Reflectance (UATR) polarization accessory in the spectral range of 4000-500 cm^{-1} at the resolution of 4 cm^{-1} for 20 accumulations per analysis.

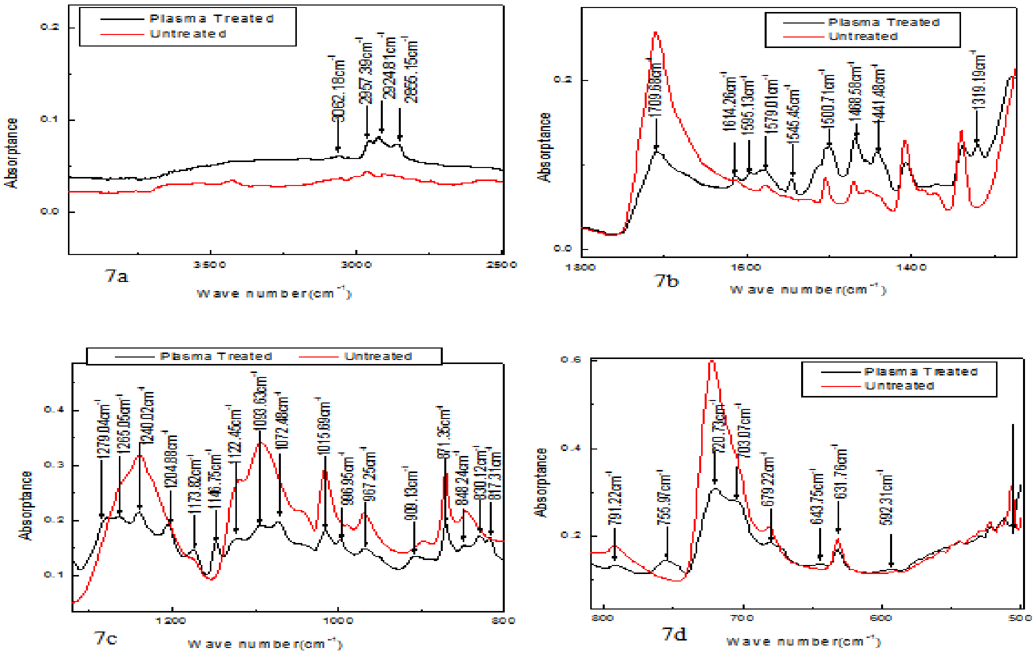

Fig.7 ATR-FTIR spectrum of plasma treated and untreated PET surface

The ATR-FTIR spectrum of the PET samples before and after 30s APPJ treatment at a distance of 3.5cm from nozzle for applied voltage 3.5kV and frequency 27kHz are shown in Fig. 7(a, b, c and d). For easy comparison between virgin and plasma treated sample, the ATR-FTIR spectrum is presented in different spectral range separately.

It can be seen that untreated PET sample, red curve in Figure 7(a-d), shows typical PET spectra with very strong absorption peaks corresponding to: (i) aromatic C-H wagging at 722.57 cm^{-1}, (ii) O-C-C asymmetric stretching peak at 1096.03 cm^{-1} with splitting sub-peak at 1118.28 cm^{-1}, (iii) asymmetric C-C-O stretching, involving the carbon in aromatic ring, at 1243.65 cm^{-1}, and (iv) C=O carbonyl ester group in conjugation with the aromatic ring at 1712.95 cm^{-1}. In addition to these very strong peaks several other prominent peaks are observed in the spectrum of untreated sample such as the peak at 871.30 cm^{-1} corresponding to aromatic C-H out of plane bending, the C-H in-plane bending peak at 1017.23 cm^{-1}, and peaks due to deformation of C-H alkane at 1340.57 and 1408.64 cm^{-1}. In addition to these, some small but clear peaks that were observed in spectrum of untreated PET sample belonged to C-H bending split peak at 1451.62 and 1470.96 cm^{-1}, aromatic C-C stretching peak at 1505.63 cm^{-1} and C-H asymmetric stretching peak at 2968.90 cm^{-1}. Finally, a small peak corresponding to stretching vibration of O-H group is observed at 3429.49 cm^{-1}.

The ATR-FTIR spectrum of the atmospheric pressure plasma jet treated PET samples shows changes in the treated part of the sample. All four major peaks of untreated samples (at 722.57, 1096.03, 1243.3 and 1712.95 cm^{-1}) not only showed the significant reduction in the peak intensity but also the emergence of sub-peaks which indicates the chain scission of PET by partial-breaking of aromatic C-H, O-C-C and C=O bonds in the exposed samples. It may be noticed that some peaks which were relatively weaker in non-treated sample now appear to be stronger, which can be attributed to the different degree of chain scission of different bonds in PET. One of most noticeable difference in plasma treated sample is emergence of a broad hump and increase in intensity of well-defined absorption peaks in region from ~3800cm^{-1} to about 2500cm^{-1} which is attributed to OH bond. This means that hydroxyl group bonding configuration in the polymer chain has increased after plasma treatment. The peak at 3429.49 cm^{-1} seems to merge with in this broad hump. Even though the argon plasma jet was used but the presence of highly reactive oxygen in atmospheric conditions might be responsible for this. Hence in can be hypothesized that the increase in oxygen content leading to a large amount of oxygen polar functional groups on the surface of plasma-treated PET may be the important reason for improving the wettability of PET

VI. Conclusion

Atmospheric pressure argon plasma has been produced and characterized by optical and electrical methods. Average electron density (n_e) by electrical method and optical method were found to be 1.546×10^{16} $cm^{-3}$and 3.42×10^{16} cm^{-3} respectively and average electron temperature (T_e) was found to be 0.37eV at the jet length of 3.5 cm from the nozzle. After Atmospheric pressure argon plasma jet treatment on PET surface, the water contact angle decreased and surface energy increased indicating improvement on hydrophilicity. It is mainly due to the increase in the polar component of the surface free energy after plasma treatment. The introduction of oxygen- containing hydrophilic polar groups into the surface was verified by FTIR spectra. It was also found that the water contact angle decreased with the increase of treatment time and surface energy increased with the increase of treatment time, and both of them reached saturated value at certain treatment time. The optimum values of water contact angle and surface energy observed on the PET surface after treatments were 24.98° and 69.4mJ/m^2,which were obtained after treatment of 60s, at distance of 3.5cm from the nozzle with applied voltage 3.5kVand frequency 27 kHz.

VII. Acknowledgements

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R. Shrestha " Experimental Study of Atmospheric Pressure Argon Plasma Jet and Surface Treatment of Polyethylene Terephthalate"International Journal ofEngineering Science Invention (IJESI), Vol. 08, No.10, 2019, PP 74-80