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Improvement of hydrophilicity of polyamide using atmospheric pressure plasma jet

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ABSTRACT

Atmospheric Pressure Plasma Jet (APPJ) has many applications in material processing such as surface modification and biomedical material processing. APPJ has been generated by a high voltage power supply (0-20 KV) at an operating frequency of (20-30) 23 kHz. This paper reports the generation and characterization of APPJ in Argon environment and its application in the surface modification of polymeric materials. The discharge has been characterized by optical and electrical methods. In order to characterize the plasma jet, its electron temperature and electron density has been determined by optical emissions spectroscopy. The surface properties of the untreated and plasma treated Polyamide (PA) samples were characterized by contact angle measurement and surface energy analysis.

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1. Introduction

Atmospheric pressure plasma technology offers an attractive perspective in today's industrial processes due to the elimination of expensive vacuum equipment, easier handling of the samples. Therefore, in recent years a lot of effort has been invested in the development of non-thermal plasma reactors working at atmospheric pressure [1]. The plasma technology is gaining a reputation as one of the most effective tools for a wide range of applications. Plasma is produced and sustained usually to a high voltage power supply at different pressures. The theoretical measurement of various plasma parameters is possible for the accuracy of the experiment. Plasma parameters such as electron temperature and density have to be calculated [2]. Different pressure plasma sources have been used for polymer surface treatment [3]. Plasma consists of ions, free electrons, free radicals, excited species, photons, and neutrals. One of the important areas of application of atmospheric pressure plasma is in the surface treatment of polymers to improve their hydrophilicity [4]. The simplest definition of a

polymer is a useful chemical made of many repeating units. A polymer can be a three-dimensional network or a two-dimensional network or a one-dimensional network [5]. Atmospheric pressure plasma jet treatment of polymers brings an effective and versatile surface modification by removing volatile impurities, increasing surface roughness, breaking of C - C and C - H bonds to form the stable linking surface structure and producing particular functional groups[6]. Polymer surface modification by discharge plasma such as plasma jet is of great industrial application and drastically enhanced wettability of polymer surface by introducing special functional groups like the carbonyl (-C=O), carboxyl (-COOH), hydroxyl (-OH) on the polymer surface after treatment [7,8]. Because of high strength to weight ratio, good resistance to corrosion, good transparency, their relatively low cost, polymers have been used to replace traditional engineering materials. However, polyamides are somewhat hydrophobic, low-surface energy materials, and thus do not adhere well to other materials. Due to its low hardness, low scratch resistance and degradation by UV radiation made surface modification possible without changing the bulk properties [9].

2. Experimental Setup

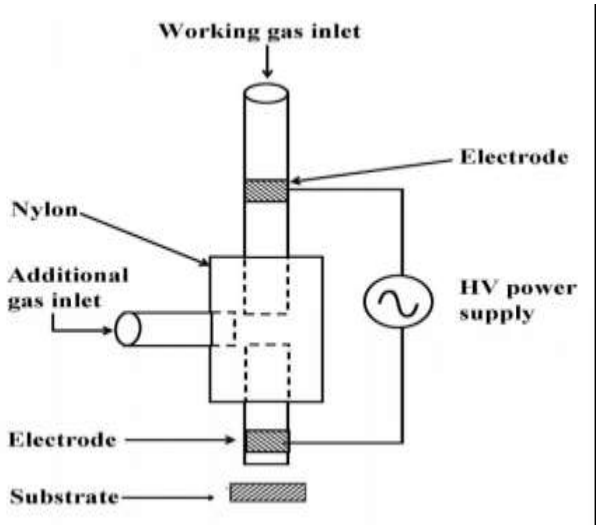

Fig.1: Schematic diagram of the experimental setup to produce plasma jet.

Fig. 1: Shows the schematic diagram of the experimental setup to produce plasma jet. The experimental setup consists of capacitively coupled electrode system made of aluminum foil of 3 mm diameter wrapped around two ordinary glass tube of outer diameter 4 mm and inner diameter 3 mm. The aluminum electrode is connected to high voltage power supply and the glass tube is coupled with nylon coupler of length 50 mm which has fine bore of 5 mm. The distance between two electrodes is fixed at 80 mm and the distance between the tip of the nozzle and lower electrode is 3 mm. The system consists of one additional inlet with a third tube connected with nylon coupler horizontally in the middle as shown in Fig.1. This third inlet can be used to introduce additional gas into the system. Argon is used as a main working gas in the experiment. The flow rate for Argon gas is 2.5 ltr/min and the voltage and the frequency were maintained at 3.5 kV and 23 kHz respectively. The samples were provided by U.K. Before treatment, removal of organic contaminants from the surface of the specimens were done by rinsing in isopropyl alcohol for 10 minutes. The samples were then ultrasonically cleaned in distilled water for 20 minutes and after that dried at room temperature. In this work, to check the homogeneity of treatment, the contact angle measurement was made at least five different locations of the samples. The average value of the contact angle thus obtained was used for the surface energy calculation.

3. Results and Discussions

Optical characterization of APPJ

Fig. 2: Shows the spectra of the discharge and their corresponding intensities and wavelength using argon as a working gas. The optical characterization of the discharge was carried out by using the line intensity ratio method. In this method four suitable lines (two for Ar I and two for Ar II) were chosen from spectral lines of argon obtain from the discharge. The working formula used to calculate the electron temperature is as follows: [10].

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

Here, in equation (1), 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 $i \rightarrow j$, 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.

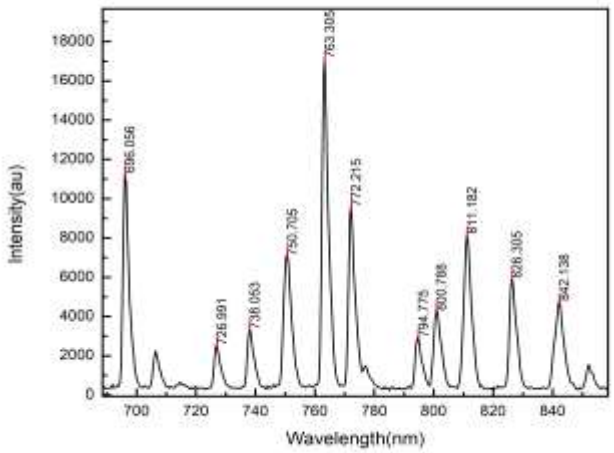

Fig.2: Spectra of the discharge at 3.5 kV with frequency 23 kHz.

The corresponding values of the transition probability, statistical weight and energy levels for the Argon I and II lines were obtained through NIST database.

Table 1: Electron temperature and their corresponding intensity ratio.

Electron Temperature (T_e) (eV)	Ratio of the intensity of Spectral lines (R_1/R_2)
0.5	1.57256
0.6	1.27136
0.7	0.98976
0.8	0.64225
0.9	0.31240
0.95	0.14225

Table 1: Shows the values of intensity ratio of spectral lines at various electron temperature.

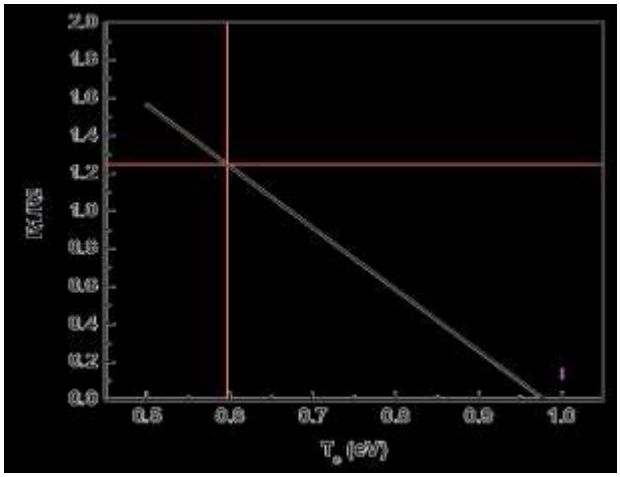

Fig.3: Graph of ratio of intensities(R_1/R_2)as the function of electron temperature(T_e)

Fig.3: Shows the graph of ratio of intensities of spectral lines with the corresponding electron temperatures.

From the graph, the electron temperature (T_e) was found to be 0.59 eV.Similarly, the electron density was calculated by using the formula expressed in equation (2).

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

The electron density was found to be $n_e = 2.1 \times 10^{16}$ cm^{-3}.

Surface modification of Polyamide (PA)

Contact angle and Surface energy measurements

The water contact angle and surface free energy are measured at the equilibrium condition according to the Young's equation and Owens Wendt Kaeble methods respectively [11].

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

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 model i and j,

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

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

Substituting the known values of the surface tension and its polar and dispersion components of the test liquids, components of surface free energy of the solid, γ_s^p and γ_s^d can be determined. The sum of these two quantities gives the total surface energy of the solid.

The treatment of the PA sample was performed for various exposure times from 5sec to 120 sec. The influence of this parameter on the hydrophilicity was investigated by contact angle measurement using a rame-hart Contact Angle Goniometer taking two test liquids (water and glycerol) on the surface of the PA. Initially contact angle of the untreated PA for water and glycerol was $51.27^0$and 47.4^0but after plasma treatment contact angle was effectively reduced to 15^0 and 24^0 respectively and become saturated after the treatment time 30 sec as shown in Fig.4 [12]. The reduction in contact angle might be due to increase roughness on the surface of PA [13].

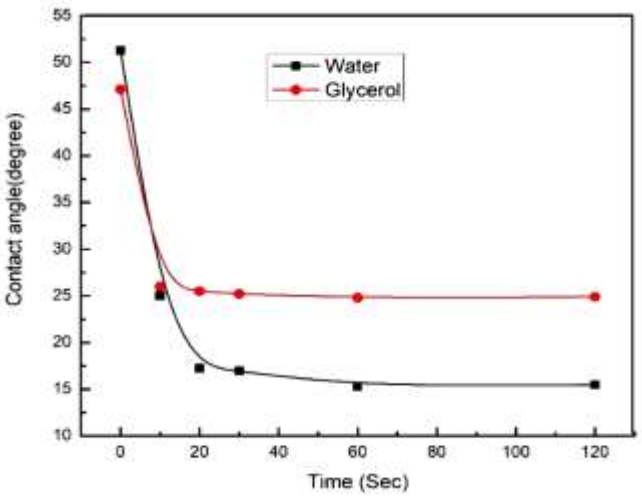

Fig.4: Variation of contact angle with the fuction of treatment time.

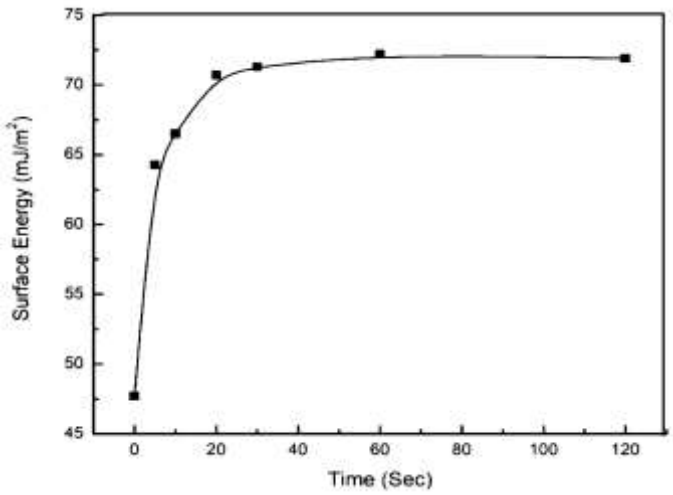

Fig. 5: Variation of surface energy with the fuction of treatment time

The variation of surface energy with treatment time is shown in Fig.5. Total surface energy increases from 47.8 mJ/m^2 to 72.5 mJ/m^2 during 120 sec treatment time. 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 [14, 15].

4. Conclusion

Atmospheric pressure argon plasma jet has been produced and characterized by optical method. Electron density (n_e) and electron temperature (T_e) were found to be of the order of $2.1 \times 10^{16} cm^{-3}$ and 0.59 eV respectively using intensity ratio method. Treatment of PA using atmospheric pressure plasma jet resulted in 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. During the experiment, contact angle of polymers after plasma jet treatment was found to decrease effectively whereas corresponding surface free energy was increased. This system is suitable for the treatment of various polymeric materials.

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