

Surface Modification of Polypropylene by Atmospheric Pressure Cold Argon/Oxygen Plasma Jet

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Abstract- Atmospheric pressure plasma jets have been established as suitable sources of low-temperature and non-equilibrium plasmas. In this paper, an atmospheric pressure plasma jet sustained in oxygen/argon mixture has been used to modify the surface properties of Polypropylene (PP). The surface properties of the untreated and plasma treated PP samples was characterized by using a ramhart contact angle goniometer. Two different test liquids distilled water and glycerol was used and the surface energy of the PP samples was determined by Owen wendtkadble method. The effect of frequency of applied voltage, the distance between sample and nozzle, and treatment time was investigated. Result showed that the water contact angle on PP reduces from 85.2° of control sample to 40° after 120s of plasma exposure. For Ar plasma jet, the contact angle decreases with increase of the discharge frequency. For O₂/Ar mixture plasma jet, the contact angle decreases with increase of discharge frequency up to 27 kHz, however, further increase of discharge frequency does not show further decrease in the contact angle at same applied voltage. At the same discharge frequency, the contact angle after O₂/Ar mixture plasma treatment is found to be much lower compared to the case of pure Ar. Moreover, it was found that, the best plasma treatment can be obtained with applying 27 kHz frequency of the source and a distance of 3.5 cm between PP samples and nozzle of the jet. A chemical modification of the PP surfaces was investigated with Attenuated Total Reflectance Fourier Transform Infrared (ATR/FTIR) spectroscopy. FTIR analysis of the plasma-treated PP films showed that plasma

treatment introduces hydrophilic functional groups on polymer surface. Thus APPJ in oxygen/argon can effectively modify the surface property of the polymers leading to enhance hydrophilicity.

Keywords- Plasma jet, contact angle, surface energy, ATR/FTIR

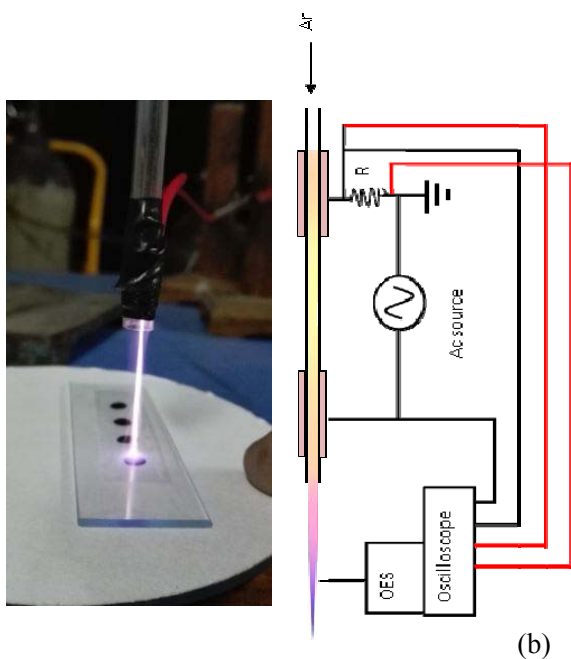
I. INTRODUCTION

Polypropylene is one of the most widely used commercial commodity polymers because of excellent physical properties, chemical resistance and good mechanical properties [1]. It is used for biomedical applications in the form of syringes, surgical sutures, blood transfusion bags and hemodialysis membranes [2]. But its poor surface properties due to its low surface energy limit their use in biomedical applications. The low surface energy of polymers results a low wettability, poor adhesion of additional coatings which have created numerous important technical challenges to be overcome by manufacturers. So it is necessary to change or improve the some of the surface properties without altering the bulk properties. Conventional methods of surface modification such as chemical treatment [3], mechanical roughening [4] and treatment with the flame [5] suffer from the problem of uniformity, reproducibility and cost effectiveness. But plasma surface modification of polymers offers a uniform, economic and environmentally friendly alternative [6,7].

Atmospheric-pressure, non-equilibrium plasmas produced by the dielectric barrier discharge are very attractive for various industrial applications because of their low-cost, high speed and the ability to operate without vacuum [8,9]. But it has small inter-electrode distance and limits the size of the object to be treated.

In this paper, we will show a new atmospheric pressure cold plasma jet generator which is excited by a frequency in the range of (2–30 kHz) AC power supply. Polypropylene film samples were treated in atmospheric pressure cold plasma jet in argon / oxygen environment. Surface analysis and characterization of the samples were performed using contact angle measurements and FTIR spectroscopy.

II. EXPERIMENTAL SETUP



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. Photograph and

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 in the range (1-30kHz) and voltage in the range of (0-20 kV) for the excitation and sustaining the discharges.

III. ELECTRICAL AND OPTICAL MEASUREMENTS

The voltage applied to the discharge was measured using a 10:1 voltage probe (Tektronix 2000TDS), and the discharge current was recorded by using a current probe. Further, a digital oscilloscope (Tek-tronix TDS2000) was employed to obtain the voltage and current waveforms.

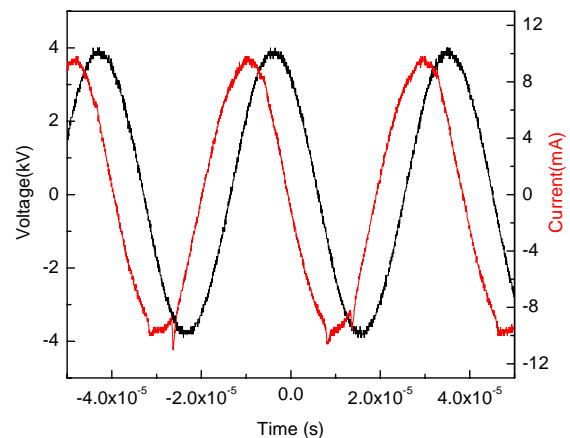


Fig 2: Current and voltage wave form of discharge

The typical waveforms of the voltage and current obtained at argon/oxygen flow rate of 2l/min are shown in Fig. 2. The peak voltage and current are approximately 3.5 kV and 10mA measured by the high voltage and current probes.

From the current wave form we can compute the average current density J_{ave} using the expression

$$J_{ave} = \frac{I}{A} \dots \dots \dots (1)$$

Where, $A = \frac{\pi d^2}{4}$ is the cross sectional area of the plasma, d is diameter of the plasma jet. For the diameter we took the value of $d = 3$ mm.

The electron density can be estimated from current density by using the expression [7, 8]

$$J = n_e e \mu E \dots\dots\dots(2)$$

where e is the elementary charge. For the electron mobility we use $\mu = 3 \times 10^{-2} \text{ m}^2/\text{V}$ [7] [36]; the strength of the electric field $E = \Delta V/D$ is calculated by taking $\Delta V = V$, i.e. the voltage drop equals the amplitude. D is the distance between the electrodes.

In our experiment

$$D = 15\text{cm}, \quad V = 3.5\text{kV}, \quad I = 10\text{mA}$$

$$E = \frac{V}{D} = \frac{3.5 \times 10^3}{15 \times 10^{-2}} = 2.333 \times 10^4 \text{Vm}^{-1}$$

$$A = 7.0714 \times 10^{-6} \text{m}^2$$

Inserting these values in equation 2, electron density was calculated and found to be $n_e = 1.105 \times 10^{13} \text{cm}^{-3}$. The optical emission spectrum (OES) was collected perpendicular to the jet using an Optical Spectrometer (Lyner Array VS140) spectrometer (spectral range of 180-1100 nm) with a resolution of 0.2 nm full width at half-maximum (FWHM); The OES data were achieved by using a per-sonal 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 position of the plasma jet (3.5 cm from the end of the torch), through an optical fiber with a diameter of 100 μm . The experimental setup for electrical and optical measurements is shown in Fig.1

The measured optical emission spectra of the plasma jet are shown in Figure 3. The most intensive emission lines of the discharge were the argon (Ar I) emission (4p \rightarrow 4s) lines in the spectral region 690–860 nm, the 2nd positive system N₂ emission bands (300–440 nm) and the transitions of the OH band between

306–309 nm. The ionic argon lines (Ar II) between 410–650 nm. The detected OH band between 306-309 nm indicates the presence of the water in the plasma. We assume that the source of the water is the ambient air, which penetrates by the diffusion into the working gas.

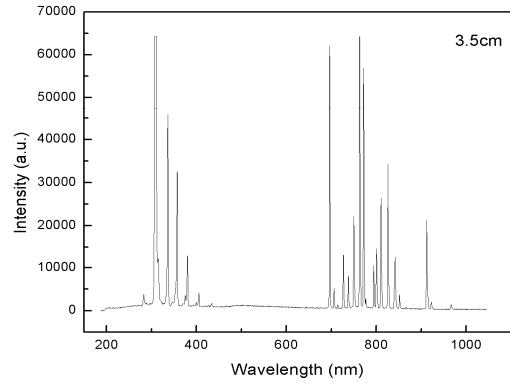


Fig.3: Optical emission spectra of APPJ at position of 3.5cm from nozzle

Based on the Ref.[9,10], the electron temperature of atmospheric pressure plasma jet can be calculated by Boltzmann plot with the equation:

$$\ln\left(\frac{I_{ki} \lambda_{ki}}{g_k A_{ki}}\right) = -\frac{E_k}{k_B T_e} + C \dots\dots\dots(3)$$

Where A_{ki} is the transition probability, T_e is the electron temperature, λ_{ki} is the wavelength, E_k and g_n are the excitation energy and the statistical weight of the upper energy state respectively. I_{ki} is the relative intensity of the chosen spectral lines, k_B is the Boltzmann constant and C is a constant for all selected spectral lines.

Now, plotting Eq. (3) with E_k in the horizontal axis and $\ln(I_{ki} \lambda_{ki} / g_k A_{ki})$ in the vertical axis will result in a straight line, and the electron temperature can be determined from the slope of the straight line.

In our experimental spectra, four ArI lines with wavelengths 696.54, 706.72, 810.64 and 912.29nm respectively were chosen in a wavelength range of 696.54–912.29 nm to calculate electron temperature of Atmospheric pressure plasma jet on the Boltzmann plot method. The atomic data of four ArI lines are displayed in table I given below.

Table I
Parameters of the four chosen ArI lines
[Taken from NIST Atomic Data]

λ nm	A_{ki}	E_i (eV)	E_k (eV)	g_i	g_k
696.54	3.39×10^6	11.548	13.327	5	3
706.72	3.80×10^6	11.548	13.302	5	5
810.64	2.50×10^7	11.623	13.153	3	3
912.29	1.89×10^7	11.540	12.907	5	3

Fig.4 is the plot of $\ln(I_{ki}\lambda_{ki}/g_k A_{ki})$ versus E_k , the slope of Boltzmann fitted straight line provides electron temperature. Electron temperature of the plasma jet for applied voltage 3.5kV with frequency 27 kHz is 0.546eV.

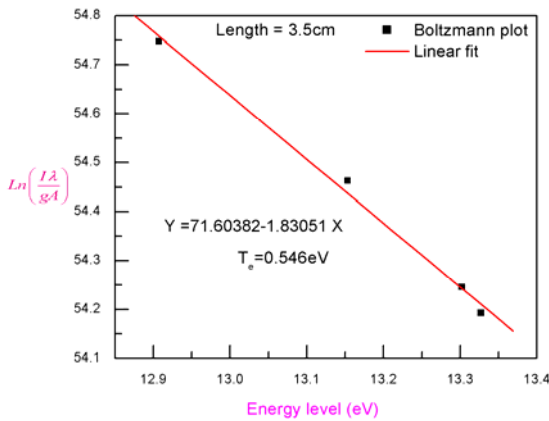


Fig.4: Boltzmann plot of the ArI line spectrum for 696.54, 706.72, 810.64 and 912.29nm

IV. MEASUREMENT OF CONTACT ANGLE AND SURFACE ENERGY

The APPJ is facing vertically downwards towards a polypropylene (PP) with a thickness of 100 μm (Good fellow Cambridge Ltd) sample surface. The distance between the APPJ nozzle and the sample was 3.5cm. The change in the surface properties of the treated PP films was monitored by measuring the change in wettability using a contact angle analyser. It consists of a camera that looks across the polymer surface, and a syringe with a needle tip to drop droplets of water onto the surface. Images from the camera are used to

measure the contact angle between the water droplet and the PP surface Contact angles, immediately after plasma treatment, was measured on PP 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 PP. 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) [11,12].

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

The dependence of contact angle and surface energy on exposure time for polypropylene is introduced in Fig: 5.

For a fixed applied voltage, flow rate of gas 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.5. 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.

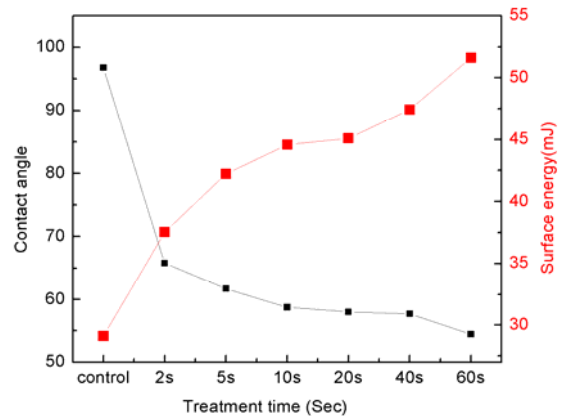


Fig.5 Contact angle and surface energy as function of treatment time

V. SURFACE ANALYSIS OF PP

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 PP was characterized by Fourier Transform infrared (FTIR) Spectroscopy.

The ATR-FTIR spectroscopy measurements of PP foils were performed with Perkin Elmer 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.

The infrared absorption spectra of untreated and plasma-treated PP fibers are shown in Fig. 6. Plasma-treated PP fiber has developed distinct absorption bands at 1548 cm^{-1} and 1697 cm^{-1} , corresponding to COO- and C=O stretching vibration, respectively, and a weak and broad absorption is also observed between 3500 and 3700 cm^{-1} , corresponding to -OH stretching vibration. In addition, it can be found that the infrared absorption spectra of the plasma-treated PP exhibits new absorption peaks at 1746 cm^{-1} and 1829 cm^{-1} . Apparently, the hydrophilic groups such as -OH, C=O, and COO- can improve the hydrophilicity of polymer [13, 14]

VI. CONCLUSION

Atmospheric pressure argon plasma has been produced and characterized by optical and electrical methods. Average electron density (n_e) by electrical method was found to be $1.105 \times 10^{13} \text{ cm}^{-3}$ and average electron temperature (T_e) was found to be 0.546 eV at the jet length of 3.5 cm from the nozzle.

The set of experimental results on the surface treatment of polypropylene (PP) film with atmospheric pressure argon/oxygen plasma jet (APPJ) using frequency (27 kHz) proves that this kind of discharge is a convenient and efficient source of non-thermal plasma.

The results of the current study showed that the atmospheric pressure plasma jet produced from argon/oxygen significantly decreased the static water contact angle and increased the surface free

energy of polymer which leads to increased wettability.

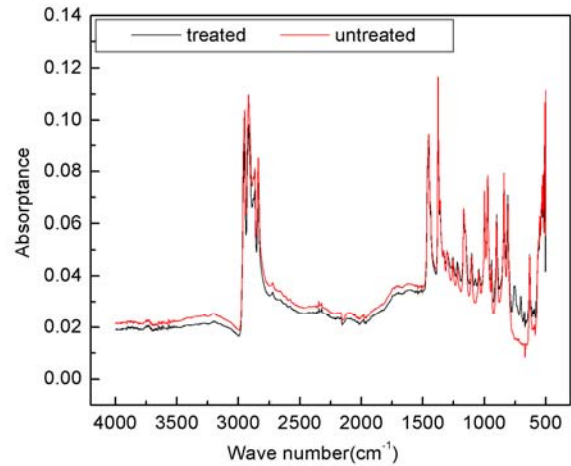


Fig.6 Infrared absorption spectra of untreated and plasma-treated PP fibers

Moreover, the introduction of oxygen-containing hydrophilic polar groups into the surface was verified by FTIR spectra.

VII. ACKNOWLEDGMENTS

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VIII. REFERENCES

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