Research Article

Cold Atmospheric Pressure Plasma Jet for the Improvement of Wettability of Polypropylene

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Received 10 March 2020; Accepted 28 May 2020; Published 20 June 2020

Academic Editor: Huining Xiao

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This paper reports the generation of cold plasma jet working under atmospheric pressure condition, for surface treatment of polymeric films. The discharge has been characterized by electrical and optical methods. The electrical property of the discharge has been studied by taking current-voltage wave forms using voltage and current probes. The production of argon plasma jet is done in atmospheric conditions which are relatively much cheaper, convenient, and safer to use. The atmospheric pressure plasma jet sustained in pure argon has been used to improve wettability of polypropylene (PP). Cold atmospheric pressure plasma jet (CAPPJ) has been generated by a high-voltage power supply (5.5 kV, 0–20 kV) at an operating frequency of 20 kHz. The surface properties of the controls and plasma-treated PP samples were characterized by contact angle measurement, surface free energy measurement, scanning electron microscopy, and the Fourier transform-infrared spectroscopy analysis.

1. Introduction

In the last two decades, plasma treatment of wood plastic composite (WPC) has been gaining popularity as a surface modification technique. WPC is a material composed of polymer plastic and wood fiber as a raw material. Polymer plastic has high strength for many structural designs, highly used in decoration and wood plastic building due to excellent processing anticorrosion and water resistance [1]. Plastics are both natural and synthetic; specially, synthesized plastic contains ester groups, and benzene ring can interact with polymer chain which brings compatibility then increases the intermolecular spacing. The cold plasma treatment effect has been used for improving the wettability on the polymer surface [2–4]. An effort has been made to electrically characterize atmospheric pressure argon plasma jet with respect to applied voltage and frequency to understand the dynamic behavior of discharge. The plasma jet is generated with a

capacitive coupled dielectric barrier discharge and a working gas of argon flowing out into the environmental air [4–6]. The produced cold plasma jet has a variety of applications in biological sectors which is harmless for human because of its low voltage and can be used clinically [7, 8]. In order to characterize the plasma jet, its electron temperature and its composition have been determined by means of optical emission spectroscopy [9, 10]. Polypropylene is a synthesized plastic which is innately hydrophobic, is low-surface energy, and thus does not adhere well to other materials; hence, it is necessary to modify their surface properties to enhance the wettability of polymeric materials [11–13]. The application of plasma jet to the treatment of polymeric materials has become increasingly important and is used to increase the adhesion strengths from control to plasma-treated samples by incorporation of oxygen-containing polar functional groups on the surface of polymers [14–16]. Surface modification by cold plasma is responsible for

FIGURE 1: Schematic diagram of the experimental setup and image of the discharge.

modifying the surface properties without changing the bulk properties of the polymers by incorporating particular polar functional groups such as carbonyl ($-\text{C}=\text{O}$), carboxyl ($-\text{COOH}$), and hydroxyl ($-\text{OH}$) on the polypropylene surface [17–21].

2. Materials

Figure 1 shows the schematic diagram of the experimental setup and image of the discharge. The experimental setup consists of electrode system made of copper foil of thickness 0.15 cm wrapped around a quartz tube with an outer diameter of 0.5 cm and an inner diameter of 0.4 cm. A high-voltage power supply (0–20 kV) was applied across the copper electrodes. The interelectrode distance is fixed at 8 cm, and the distance between the tip of the nozzle and grounded electrode is 0.3 cm. Argon was used as the main working gas in the experiment. The flow rate for argon gas was 3 L/min, and the voltage and frequency were maintained at 5.5 kV and 20 kHz (operating frequency), respectively. Electrical characterization of the discharge was done with the help of the TEKTRONIX TDS2002 oscilloscope by measuring the current and voltage waveform with current probe and voltage probe (PINTEX HVP-28HF), respectively. The attenuation ratio of the voltage probe was 1000:1. The current waveform was measured by placing a current probe across a shunt resistor of 10 k Ω . The Rame-Hart goniometer (model 200) was used for the measurement of contact angle of the control and plasma-treated polypropylene films. The ATR-FTIR spectroscopy measurements on polymer foils were performed with a Perkin Elmer Spectrum 100 FTIR spectrometer fitted with the Universal Attenuated Total Reflectance (UATR) polarization accessory in the spectral range of 4000–500 cm^{-1} at a resolution of 4 cm^{-1} for 20 accumulations per analysis. The LEO (500)/Zeiss field-emission scanning

electron microscope (SEM) was used to check the surface roughness of polymeric materials.

3. Methods

The power balance method was used for the estimation of electron density. Similarly, optical characterization of the discharge was done using the Stark broadening method and the Boltzmann plot method with the help of an optical emission spectrometer (USB 2000+, Ocean Optics). The samples of polymeric films (PP) were treated by plasma jet by placing it vertically 2.5 cm below from the tip of the nozzle. Samples of PP with dimension 60 mm $\times$ 20 mm $\times$ 0.05 mm were used. The samples were provided by Goodfellow, UK. Before treatment, removal of organic contaminants from the surface of the specimens was done by rinsing in isopropyl alcohol for 10 min. The samples were then ultrasonically cleaned in distilled water for 15 minutes and after that dried at room temperature in a clean environment. The contact angle measurements were done at five different locations on the same sample, and the average value of the contact angle obtained was used for the surface energy calculations.

4. Results and Discussion

4.1. Temperature of Atmospheric Pressure Plasma Jet. The atmospheric pressure plasma discharge approximately matches with the surrounding atmosphere. This plasma is also called normal plasma. The plasma jet was designed with locally available materials to make treatment continuous and cost effective. Temperature of plasma jet was experimentally found to be about 27°C at 5.5 kV. So, it is called cold atmospheric pressure plasma jet and is widely used for the surface modification of polypropylene.

FIGURE 2: Current-voltage graph at gas flow rate $Q = 3$ L/min at an applied voltage of 5.5 kV.

4.2. Electrical Characterization of APPJ. The total power consumed by a plasma jet can be written as $P_{av} = 2An_e v_b E_{lost}$, where $2An_e v_b E_{lost}$ represents the total power of the discharge over the area $2A$ of the two electrodes and v_b being the Bohm velocity. Therefore, the expression for electron density is

$$n_e = \frac{P_{av}}{2Av_b E_{lost}}. \quad (1)$$

This equation can be used to determine the electron density in the glow mode of the discharge [22].

Figure 2 shows the current and voltage waveforms of APPJ generated in argon with an electrode gap of 8 cm and an applied voltage of 5.5 kV at an atmospheric pressure condition. Using the values of applied voltage and average discharge current, the electron density is determined using equation (1). Putting the value of the Bohm velocity $v_b = 2 \times 10^3$ m/s, energy lost 80×10^{-19} Joule, electrode area 4.096×10^{-5} m², applied voltage 5.5 kV, and discharge current about 25 mA, the electron density was found to be $n_e = 7.6 \times 10^{16}$ cm⁻³. The power consumed per cycle was about 137.5 Watt.

4.3. Optical Characterization of APPJ

4.3.1. Stark Broadening Method. The emission spectra of the discharge were also used to measure electron density, using the Stark broadening method [23, 24].

Figure 3 shows the optical spectrum (left) and its Lorentzian fit (right) of the data for the line. In this method, the prominent argon line at 696.54 nm was chosen for the estimation of electron density. The full width at half maximum

(FWHM) of the Stark broadening $\Delta\lambda_{\text{Stark}}$ is related to the electron density represented by equation (2).

$$\Delta\lambda_{\text{Stark}} = 2 \times 10^{-11} n_e^{2/3}. \quad (2)$$

From the FWHM method, the calculated value of $\Delta\lambda_{\text{Stark}}$ is obtained (1.65 nm) and putting this value in equation (2), the corresponding electron density (n_e) was found to be about 2.27×10^{16} cm⁻³.

4.3.2. The Boltzmann Plot Method. For the determination of electron temperature, the discharge was diagnosed by using the Boltzmann plot method. In this method, seven suitable lines of Ar I were taken from the spectral lines of argon plasma discharge. The working formula used to calculate the electron temperature is expressed in equation (3) as follows [25].

$$\ln \left[\frac{\lambda I}{hcA_{ji}g_j} \right] = -\frac{E_j}{kT_e} + C. \quad (3)$$

A plot of the above equation with E_j on the horizontal axis and $\ln(\lambda I/hcA_{ji}g_j)$ on the vertical axis was made which resulted in a straight line, and the electron temperature (T_e) was obtained from the slope of the straight line which is shown in Figure 4.

From Figure 4, the electron temperature was found to be of the order of 1.03 eV, which corresponds to an electron temperature of about 11845° Kelvin.

4.4. Surface Modification of Polypropylene

4.4.1. Contact Angle and Surface Energy Measurements. In a homogeneous surface, the water contact angle and surface

FIGURE 3: Spectrum of the discharge at 5.5 kV with a frequency of 20 kHz in argon (flow rate = 3 L/min).

energy were determined according to the Young equation and the Owens-Wendt methods, respectively [26, 27].

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}. \quad (4)$$

Here, γ_{sv} is the surface free energy of the solid substrate, γ_{sl} is the interfacial free energy between the solid and the liquid, and γ_{lv} is the surface tension of the liquid.

In the case of two liquids i and j ,

$$\gamma_{li}(1 + \cos \theta_i) = 2 \left(\gamma_{li}^d \gamma_s^d \right)^{1/2} + 2 \left(\gamma_{li}^p \gamma_s^p \right)^{1/2}, \quad (5)$$

$$\gamma_{lj}(1 + \cos \theta_j) = 2 \left(\gamma_{lj}^d \gamma_s^d \right)^{1/2} + 2 \left(\gamma_{lj}^p \gamma_s^p \right)^{1/2}. \quad (6)$$

By using the values of the surface tension and its polar and dispersion components of the test liquids, components of the surface energy of the solid, γ_s^p and γ_s^d can be

FIGURE 4: The Boltzmann plot method for the determination of electron temperature.

FIGURE 5: Variation of the contact angle of polypropylene with treatment time.

determined from equations (5) and (6). The addition of these two quantities represents the total surface energy of the solid [28].

Figure 5 shows the variation of contact angle of PP samples with treatment time. The effect of treatment time on the wettability was investigated, using a contact angle goniometer (model 200) by using two test liquid models (water and glycerol) on the surface of the polymers. Results showed that

a vast decrease in the contact angle takes place with the treatment time up to 120 seconds. At first, the contact angles on the control sample for water and glycerol were 94.5° and 84° , but after plasma jet treatment, the contact angles were reduced to 57° and 65° , respectively, and became constant after a treatment time of 30 seconds. The reduction in contact angle might be due to the increase in roughness on the surface of PP [14, 19, 29, 30].

FIGURE 6: Variation of surface free energy of polypropylene with treatment time.

FIGURE 7: SEM images of untreated (a) and plasma-treated (b) samples of PP at 60 seconds.

Figure 6 shows the variation of surface energy and its polar and dispersive components of PP samples with a treatment time of 120 seconds. The total surface energy increases from 37 mJ/m^2 to 48 mJ/m^2 in 35 seconds. A 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), hydroxyl ($-\text{OH}$), and carboxyl ($-\text{COOH}$) groups on the polymer surface after treatment. The dispersion component does not have any contribution to increase the hydrophilicity on the polypropylene surface [13, 14, 20, 31].

4.4.2. SEM Images of the Untreated and Plasma-Treated PP. Figure 7 shows the SEM morphology of the untreated and plasma-treated polymer surface of PP at 60 seconds. The gradual increase in the particle grain size with the image scan area can be realized. The change in surface roughness of the sample after treatment was analyzed by scanning electron microscopy (SEM). SEM images of untreated and argon plasma jet-treated sample indicated that the plasma treatment produces a significant increase roughness on the surface of PP [30].

FIGURE 8: FTIR spectra of untreated and plasma-treated sample of polypropylene.

4.4.3. FTIR Analysis. Figure 8 shows the FTIR spectra of the untreated and cold plasma jet-treated samples of polypropylene. There is change in intensity of absorption peaks due to incorporation of oxygen-containing polar functional groups on the surface of polymer after plasma jet treatment. FTIR spectra shows the presence of carbonyl peaks ($\text{C}=\text{O}$) which represents surface oxidation. Previous studies have also shown a similar result that to oxidize can be confirmed due to presence of carbonyl peaks and stretching of C-H bonds at wavelengths 1450 cm^{-1} and 1375 cm^{-1} , respectively. The stretching of C-H bonds and aromatic rings were obtained at wavelengths 2862 to 2975 cm^{-1} , respectively [30–35].

5. Conclusions

The cost-effective system of generating plasma jet at an atmospheric pressure with the potential application in material processing has been developed. The temperature of the plasma jet was measured to be about 27°C at 5.5 kV . So, this discharge is termed as cold plasma and is widely used in heat-sensitive material processing. Atmospheric pressure plasma jet has been characterized by optical and electrical methods. Electron density (n_e) and electron temperature (T_e) were found to be of the order of 10^{16} cm^{-3} using the Stark broadening and power balance methods and 1.03 eV using the Boltzmann plot method. Cold plasma jet treatment of polypropylene effectively improves hydrophilicity. The contact angle of the polymer after plasma jet treatment was found to decrease whereas the corresponding surface energy was found to increase. It is due to the incorporation of polar functional groups on the PP surface after treatment. SEM images of the untreated and plasma jet-treated sample confirmed that the cold plasma treatment produces a significant improvement in the roughness of the surface of a polypro-

pylene film. The FTIR analysis concludes that there is incorporation of oxygen-containing polar functional groups such as carbonyl ($\text{C}=\text{O}$) peaks and stretching of C-H bonds on the surface of polypropylene which indicates the improvement of the wettability on the PP surface.

Data Availability

The data (figures) that support the findings of this study are available upon request from the corresponding author.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this research article.

Acknowledgments

The corresponding author was supported by the Nepal Academy of Science and Technology (NAST), Nepal, by providing a Ph.D. fellowship through Grant No.: 11/073/074. The authors would like to acknowledge Tri-Chandra Multiple Campus, Tribhuvan University, Institute of Science and Technology (IOST), Nepal for their invaluable help and support. The authors would like to thank Prof. Andrzej Huczko from the University of Warsaw, Poland, for the SEM analysis of the polymer samples.

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