Atmospheric Pressure Plasma Helix Polyethylene terephthalate Surface Activation and Its Electron Density Measurement

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Abstract—The new helix mode of atmospheric pressure plasma discharge was used for increasing polyethylene terephthalate (PET) surface wettability and the power effect on plasma surface modification was studied. The altered PET surface wettability was observed based on static contact angle measurements and PET surface became highly hydrophilic when exposed to plasma helix. The substantial increase in PET surface wettability attributable to the crosslinking *via* activated species of inert gases effect from plasma helix was inspected. Optical emission spectroscopy was used to determine chemical species of plasma helix at one atmospheric-pressure. The correlation of plasma surface modification consequence and the electron characteristics in plasma helix with rising plasma power inputs were studied. The present results show that plasma helix is an operative plasma system that can be used to enhance polymer surface wettability.

1. INTRODUCTION

Polyethylene terephthalate (PET) can be seen as the emerging polymer which can be utilized for a variety of Manufacturing methods because of its admirable chemical and physical characteristics [1, 2]. On the other hand, the intrinsic low surface energy of PET materials rests the main weakness to its industrial use, leading to unfavorably reduced adhesion in heterogeneous integration. To overcome this issue, an operative and simple surface treatment is exactly claimed. Atmospheric pressure plasma treatment can be seen an effective alternative to existing conventional surface modifications with several advantages such as dry process and low cost system. From these features, atmospheric plasma surface modifications for the heat sensitive polymeric materials such as PET are attractive and numerous newly developed atmosphere pressure plasma sources has developed in the recent years [3–5]. Though, the plasma power inputs are not only capable to sustain plasma source, they also dominate the chemical reactions with polymer surfaces [6]. From this point of view, the electrical fields generated at power inputs cause the great potential sheaths across which ions accelerate and strike the polymer surface with high energy [7, 8]. It is essential to realize the power input and flux of the charged species has enabled the use of atmospheric pressure plasma for PET surface treatment. For this reason, it is crucial to examine the influence of power input during plasma surface treatment in detail, as PET surfaces modified in this manner exhibit changes in surface wettability [9, 10]. In contrast to many researches of vacuum plasma polyethylene terephthalate surface treatments, there are few literature reports in the electron density measurement of atmospheric-pressure plasma on PET surface modification with power effects. Therefore, we present the study of the Polyethylene terephthalate (PET) surface interaction of the new helix mode of atmospheric pressure plasma discharge with adjusting plasma power inputs. The major target of this paper is focusing on the power effects of the plasma helix on PET surface wettability. By using optical emission spectroscopy (OES), the intensities of the emitting plasma species in luminous gas phase were detected. Moreover, the transition of electron density during plasma helix on PET surface were evaluated. With this in mind, we present new helix mode of atmospheric pressure plasma discharge and describe the modification of PET surfaces with plasma power effects.

2. EXPERIMENTAL METHODS

The helix mode of atmospheric pressure plasma discharge used to treat polyethylene terephthalate (PET) is shown in Fig. 1a. This helix mode of atmospheric pressure plasma is based on the special design of carrier gas compartment to generate the rotational gas diffusion to form the helix discharge. The rotational diffusion can be seen as the process by which the equilibrium statistical distribution of the overall orien-
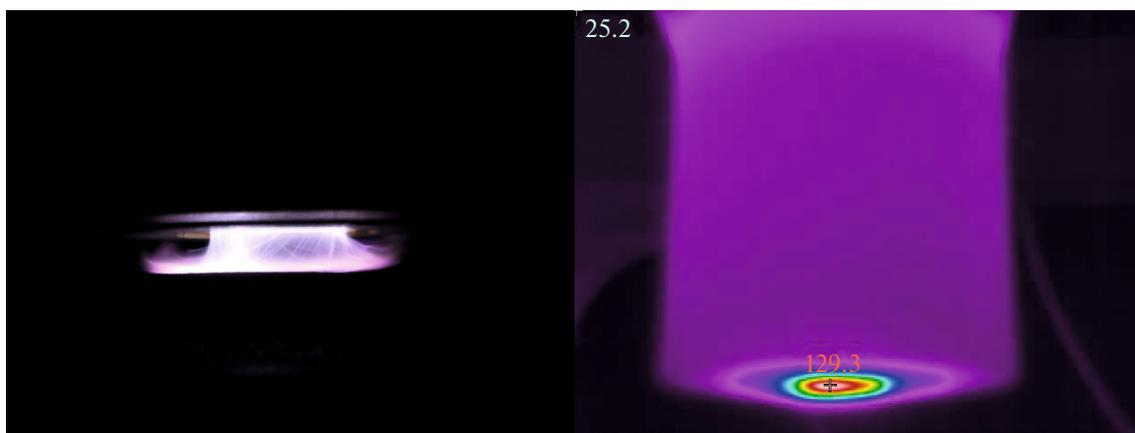
Fig. 1. (a) Luminous gas phase of plasma helix system and (b) the temperature profile of infrared thermal imaging (Plasma conditions: argon, 10 slm; RF plasma power, 80 W).

tation of gas molecules is restored. This plasma helix consists of a gas compartment and the high-speed flow of argon (7−11 slm) is introduced from the top of the plasma system and passes through the gas compartment as the ionization gas. An electrical field is applied by a 13.56 MHz radio frequency power supply to ignite the plasma helix. Figure 1a shows the diffusing glow gradually fills the reactor region and it refers that the luminous gas phase can also be stabilized by applying the enhanced gas flow to the discharge. The PET sample was mounted on an X-Y movable table to simulate in-line processing at variable line speeds. Figure 1b shows the infrared thermal imaging of plasma helix touching the substrate. The sensitivity of infrared thermal measuring technique is 150 mk at a surrounding temperature of 25.2°C. The radiant temperature profile of plasma helix measured by infrared thermal analysis was similar to those obtained from the thermocouple thermometer analysis shown in Fig. 1b.

Argon gas which used to create plasma helix plasma was an industrial grade with 99.995% purity and purchased from Min-Yang Gas Corporation. Polyethylene terephthalate (PET) samples (0.5 mm thick) were supplied by Yo-Ho Corporation. The static contact angles of PET samples were measured by projecting an image of an automatic sessile droplet resting on a PET surface with a Magic Droplet Model 100SB Video Contact Angle System (Sindatek Instruments Corporation, Taipei, Taiwan). To understand the nature of the PET surface change, the dispersion and polar interaction contributions to the surface energy of the polymer materials were calculated using the Owens-Wendt model [11]. The liquids used for calculating the surface energies of the unmodified and plasma helix treated PET samples were water and diiodomethane of known γ^p (polar component) and γ^d (disperse component). The surface energy of a solid (γ^s) has two components, namely, a polar component

and a disperse component. Both components contribute to the total surface energy:

$$\gamma_{LV}\left(1 + \cos\theta\right) = 2\left(\gamma_L^d\gamma_S^d\right)^{1/2} + 2\left(\gamma_L^p\gamma_S^p\right)^{1/2}. \quad (1)$$

To detect the photo-emitting species, and thus indirectly inspect the chemical composition of the glow discharge of the plasma helix PET surface activation, OES was used as plasma diagnostic. OES consists of both the instrumentation and spectrum analysis software, which was supplied by Hong-Ming Technology, Inc. The observable spectral range was 250−950 nm with a resolution of 2 nm. An 1 m long fiber optic cable, coupled to an immobile width (50 μm) slit. In plasma parameters, electronic excitation temperature has a vital position because it gives the information of the collision process generating active species, density of active species, and reactions in the plasma state [12]. In this study, we used the Voigt profile method based on OES to calculate the electron density during atmospheric-pressure plasma etching. The electron density from the correlation of the Voigt profile is estimated according to:

$$n_e = \left[\left(\frac{\Delta\lambda_V^2 - (1.21\times10^{-7}T_g + 3.6481)}{\Delta\lambda_V} - \frac{4.4392}{T_g^{0.7}}\right)\right.$$
$$\left.\times\frac{1}{1.96\times10^{-11}}\right]^{\frac{3}{2}}, \quad (2)$$

where $\Delta\lambda_V$ is the Voigt profile; Δn_e is the electron density; P is 1 atm; and T_g is the gas temperature. The gas temperature used in this study was 338 K, which was measured using a thermocouple thermometer and by infrared thermal imaging. A detailed description and the derivation of the electron density of argon plasma at one atmospheric-pressure were reported in previously study [13]. In this study, we used the methods based on OES to evaluate the electron density in plasma helix. Because of the numerous collisions

among the particles in the atmospheric-pressure plasma discharge, the broadenings are represented as the different broadening mechanisms including in Stark, Van der Waals, Doppler, nature, resonance, and instrument in the emission line [14, 15].

3. RESULTS AND DISCUSSION

Static contact angle measurement is one of the simplest methods used to examine surface feature variations that appear on PET surfaces with atmospheric pressure plasma helix exposure [16]. We used this method to evaluate the surface free energy of plasma helix modified PET surface. Figure 2 shows the change in the static contact-angle measurement with respect to growing plasma power inputs in plasma helix at RF power 80−160 W, argon carrier gas flow rate of 10 slm, and working distance 5 mm, 60 s. As shown in Fig. 2a, both static contact-angle values (DI water and di-iodomethane) of plasma modified PET surfaces gradually decreased with increasing plasma power input. The most efficient RF plasma power level was 160 W, for which PET surface was effectively modified. Surface free energy is the work that would be essential to increase the surface area of a solid phase and it could be recognized as the indicator which refer material surface properties. Figure 2b shows the variation in surface energy and its polar and dispersive components as a function of increasing plasma power input from 80 to 160 W. The surface free energy of the unmodified PET is 39.8 mN/m^2. The surface energy increases with increasing plasma power input. Thus, at higher plasma power input (120−160 W), the surface free energy increases from 49.8 to 60.9 mN/m^2. The increase in the power input could increase the surface concentration of polar functional groups on PET surface, as evidenced by gradual increases in the polar contribution with respect to an increase in the reactive plasma species. The abundance of reactive species in the plasma gas phase, which can react with the activated surface, is believed to positively correlate with the plasma power input. Therefore, the number of activated sites on the surface is more when the power input is high. These results also suppose that the plasma treatment with rising power input made PET surface more hydrophilic at a certain level depending on the operating conditions.

The optical emission analysis is predictable to elucidate the reactions of chemically reactive species in plasma helix that may contribute to PET surface modification. The optical emission spectra of plasma helix are shown in Fig. 3. According to these spectra, the strong Ar emission lines are dominant at approximately 700−800 nm. Regarding the strong Ar plasma species from the OES analysis, the CASING (Crosslinking *via* Activated Species of Inert Gases) effect may be responsible for the plasma helix treatment on the PET surface. Radicals released from plasma helix may have generated active sites, and these radicals

interact with the PET surface to generate dangling bonds that then lead to the formation of the surface active sites [17]. OES also detects noticeable emission lines between 300−400 nm attributable to molecular nitrogen bands, as well as emission lines at 777 and 844 nm due to oxygen atoms from the ambient air. These data indicate that atmospheric-pressure plasma helix surface modification is the result of the electron-impact-dissociation of ambient air [18]. The optical emission analysis of plasma helix suggests the possible surface modification effect of Ar, N, and O plasma species. Furthermore, the plasma surface modification can be attributed to the interaction of oxygen-based plasma species in the atmospheric-pressure plasma with polymers [19]. Oxygen-based plasma species, such as O and O$_3$ radicals, can create oxygen-containing groups *via* oxidation processes. Figure 3 also shows that the rising emission intensities can be considered to correspond to more energy production in the plasma and it is stabilized with increasing plasma power input as well. It suggests that, as expected, the surface modification effect in the plasma is enhanced when the power input is increased.

There is a need for non-intrusive, time-resolved plasma diagnostics to study atmospheric pressure plasma processing on polymeric surface. OES could be used for determining the electronic density results from the Stark broadening of measured spectral lines. The radioactive particles perturbation increase is caused by the electrical fields produced by the environmental electron and ions. In this method, the absolute intensities are not required, only the relative lines shape and width. For electron densities is 10^{14} cm^{-3}, the broadening is high, and standard spectrometers and monochromators are sufficient [20]. The electron density calculated from Gig-Card and GKS theory is shown in Figure 4 [21]. The obtained electron density ranged 9.0×10^{14} cm^{-3}~1.7×10^{15} cm^{-3} depending on the rising plasma powers input conditions. Figure 4 shows the increasing electron density with rising plasma power input at plasma modification on the PET surface. Because the intensity of the Ar* line is proportional to the population of rising plasma power inputs, the plasma power is dominated by emission from plasma helix. It is clear from graph that the electron density increases with rising plasma power input. It may be attributed to more collision of argon gas under higher plasma power input, and thus increase in electron collision frequency. This fact in turn provides enough energy for electrons to be accelerated in response of the applied field and; consequently, an increase in the kinetic energy of electrons [22]. For comparison Figs. 2 and 4, the higher electron densities were obtained at higher plasma power input to evaluate more frequently electron creation in plasma helix. From this observation, therefore, the electron evolution in plasma helix which is expressed by the electron density can be seen the minor key factor examined in the plasma helix surface modification
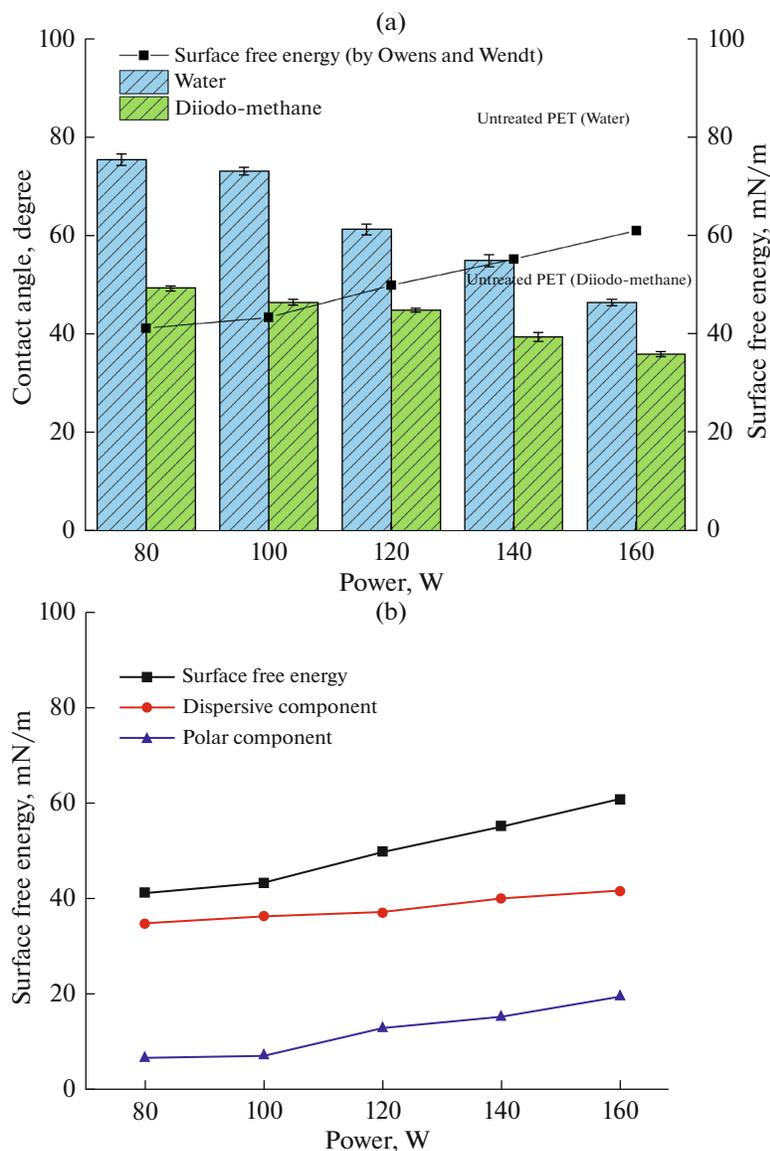
Fig. 2. (a) Average contact angle values. (b) Surface free energy changes of plasma helix-modified PET at different RF plasma power inputs.

4. CONCLUSIONS

of PET samples. The possible reason is that in common plasmas; the group of high energy electrons play an important role in excitation of argon gas, but they are unable to effectively transfer their energy to the argon gases due to; inelastic collisions with the atoms [23]. When more power inputs were added to the plasma helix, the collisions between excited argon metastable species occurred, resulting in an energy transfer to the reactive gas molecules. The direct outcome of such an energy transfer was non-production of new reactive plasma species. These plasma species thus formed also could react with the polymer surface, achieving surface modification of organic materials [24].

Polyethylene terephthalate (PET) surfaces were treated by atmospheric pressure plasma helix. The static contact angle results indicated that plasma helix rapidly improves the hydrophilicity and surface energy of PET surface. The polar functional groups generated on PET surfaces by the plasma treatment decrease the contact angle and increase the surface free energy. Optical emission spectroscopy determines the plasma reactive species from plasma helix, which contribute to PET surface modification. According to the OES analysis, the interaction of reactive plasma species in the plasma with the PET surface may enhance the surface activation. OES analysis also indicates that the amount of electronically excited species in the plasma
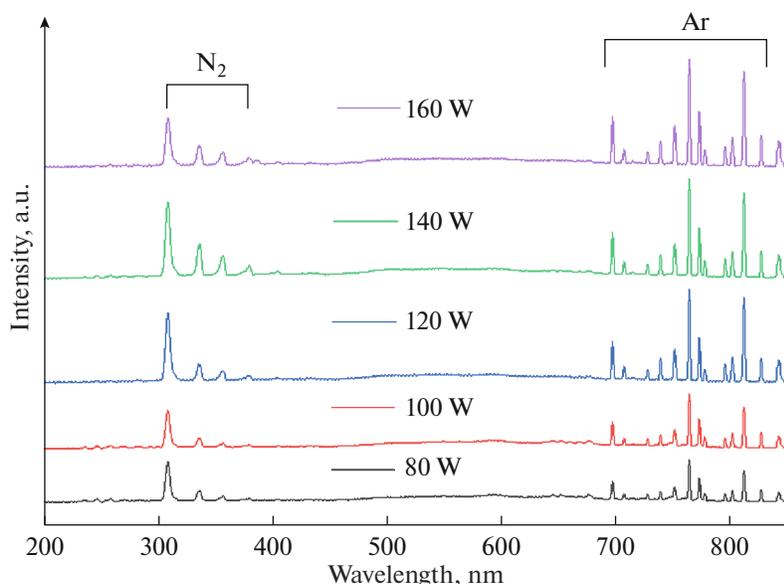
Fig. 3. The optical emission spectrum from atmospheric pressure plasma helix (Plasma conditions: argon, 10 slm; RF plasma power, 80−160 W).

helix was significantly influenced by rising power input. The increasing trend of both electron density is observed for rising plasma power input in plasma helix on PET surface. The research results proved the possibility of power input effect on plasma helix surface modification.
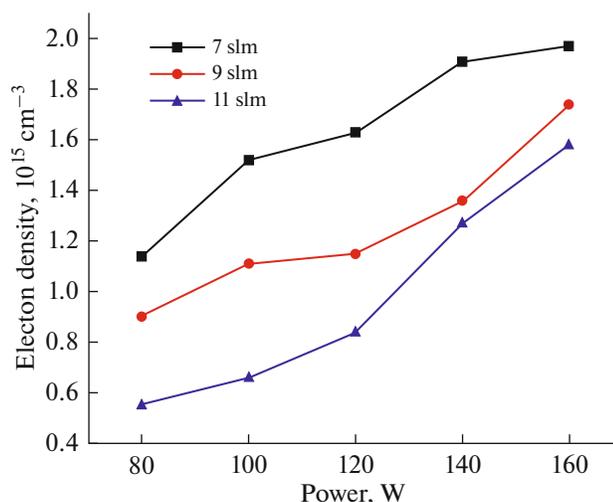
Fig. 4. The variation of electron density from atmospheric pressure plasma helix (Plasma conditions: argon, 7−11 slm; RF plasma power, 80−160 W).

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