A Simple Approach to Surface Modification Using Polytetrafluoroethylene (PTFE) with Laminar and Turbulent Flows of Micro Plasma Jets at Atmospheric Pressure

Heesoo Jung, Bomi Gweon, Dan Bee Kim, Wonho Choe*

Unlike large area plasmas, small size plasma jets could be useful in treating localized regions. For this reason, we developed a micro plasma jet having a polytetrafluoroethylene (PTFE) part exposed to the discharge inside the plasma source. As the helium gas flow rate was raised from 0.1 to 6.0 slpm, the plasma exhibited a change in characteristic from laminar to turbulent and an abrupt change of appearance at a certain flow rate (2.0–3.0 slpm). The measured rotational temperature was above 500 K under laminar flow conditions, which was a sufficiently high temperature for the pyrolysis of PTFE, and the excitation temperature of the laminar flow was higher than that of the turbulent flow. The corresponding optical emission spectra were different (CN, C₂, F₁, H₂, dominated for laminar conditions while N₂⁺, OH, OI dominated for turbulent flow conditions). These different plasma characteristics were obtained by simply controlling the gas flow rate. A feasibility study of surface modification demonstrated a change of the surface wettability from hydrophobic to hydrophilic (and vice versa) depending only on the gas flow rate.

Introduction

Atmospheric pressure micro plasma jets have recently been attempted and/or used for various applications.¹,² Inactivation of microbes and decomposition of chemical compounds are just a few prominent examples.³,⁴ In particular, plasma-aided processes such as etching and deposition using the atmospheric pressure plasmas are expected to reduce the complexity of manufacturing processes. Thus, many researchers are investigating the development of simple, convenient, and accessible methods using atmospheric pressure plasma jets to treat the surfaces of various materials.

The surface modification of materials is an important field throughout the industry.⁵,⁶ Hydrophobic coating protects the material from water, and hydrophilic effects increase the adhesion properties of the surface. Such attractive properties are desirable in many applications: water-resistant interface,⁷ titanium related material for medical applications,⁸ self-cleaning surface,⁹ microflu-
dic patterned devices,\[10,11\] cell patterning,\[12\] and polymer films.\[13,14\] Accordingly, this research topic is being actively studied in material engineering, chemical engineering, and bioengineering.\[3,5,6,8,13,15\]

A number of studies have presented fabrication methods for producing hydrophobic and hydrophilic surfaces including particle deposition, vapor deposition, sol-gel techniques, casting techniques, and plasma treatment.\[6,8,14,16,17\] Among them, atmospheric pressure plasma treatment offers an especially simple way of changing the surface properties using various supply gases. Hydrophilicity is achieved by increasing the surface energy of the surface. This may be achieved with inert gas plasmas, but more readily with plasma streams which add polar functions to the surface. Fluorocarbon plasmas (C\(_x\)F\(_y\), where \(x\) and \(y\) are integers) are used to obtain the hydrophobic polymer surfaces\[6,14,18\] while noble gases (helium, argon, etc) and nitrogen change the surface to be hydrophilic through plasmas.\[6\] Using fluorine as a supply gas in the ambient air condition for producing fluorine plasma environment, however, adds complexity due to its highly reactive property at high concentration.\[19\] Therefore, an alternative idea is required to control the fluorine component. Instead of using the chemically reactive fluorine supply gas, control of fluorine component and thus change of the surface wettability is shown in this article by utilizing an atmospheric plasma jet source including a polytetrafluoroethylene (PTFE) part attached to the powered electrode and by supplying the inert helium gas. We studied how the plasma flow transition and characteristics (visible plasma jet length, rotational and electron excitation temperatures, and dominant species analysis from the plasma emission) became altered due to different gas flow rates. We, then, found a simple and fast method to control the hydrophobic and hydrophilic properties by using the pyrolysis of PTFE in different plasma jet flows under the ambient air condition.

**Experimental Section**

**Micro Plasma Jet Structure**

A schematic of the atmospheric pressure micro jet source and an optical emission spectroscopic diagnostic setup are illustrated in Figure 1a. The shape of the copper electrode is similar to the one in other dc arc jet sources with a sharpened tip. Its length and the diameter are 50 and 5 mm, respectively. A piece of 15 mm long PTFE was inserted inside the discharge region to utilize the fluorine species produced by the pyrolysis of the material under some plasma conditions. The gas flows through a 4 mm in length and 1 mm in diameter straight channel provided by the thickness of the material near the tip of the cone shaped nozzle. The whole length of the source is 67 mm. The electrode was powered by a 50 kHz square pulse supply (FT-Lab, HPI 500) with a 50% duty cycle. The discharge voltage and current were measured using a V–I probe (ProSys), and the measured dissipated power range was between 0 and 70 W. A 99.999% pure helium gas supplied to the plasma source was controlled by a mass flow controller (Tylan FC-280SAV) and a ball flow meter (Kofloc). In order to investigate the optical emission spectra from the plasma jet, a spectrometer (Acton SpectraPro 750) was used with a charge coupled device detector (IDUS DV401A-BV). The emission spectra were acquired through an optical fiber located at 30 mm from the nozzle.

**Plasma Current–Voltage Characteristics**

Figure 1b shows the measured peak-to-peak voltage (\(\circ\), \(\bullet\)) and average dissipated power (\(\circ\), \(\downarrow\), \(\bullet\)).
This $I$–$V$ characteristic curve can be divided into four regions. The breakdown occurs at 800 V at the end of region (1), which brings about a voltage drop of about 50 V and an instantaneous increase in the current from 0.02 to 0.15 A as depicted in region (2). In region (3), the voltage increases with current which reflects the abnormal glow discharge. In region (4), however, the voltage remains almost constant while the current increases. The dissipated power in Figure 1b was obtained by

$$P_{\text{diss}} = \frac{1}{r} \int_0^t I(t) V(t) \, dt$$

(1)

where $r$ is the period of the input voltage. The average dissipated power is proportional to current more significantly after the plasma is initiated.

Results and Discussion

Flow Transition of the Mico Plasma Jet

To reduce some operational variables, the dissipated power was fixed at 50 W throughout the experiment. Figure 2 presents the images of the micro plasma jet taken by a digital single lens reflex camera (Canon EOS 500D). As seen in the figure, plasma length dramatically changes at certain helium gas flow rates. At low flow rates (<2.0 slpm), the plasma length increases up to 13.5 mm as the flow rate is increased. At high flow rates (3.0–6.0 slpm), on the other hand, the plasma length is steady at 4.5 mm, which demonstrates a transition in the 2.0–3.0 slpm flow range. This abrupt length change, similarly observed by others, is related to laminar to turbulent flow transition. In general, laminar flow occurs in parallel layers with no disruption between the layers, so high viscous force affects the flow (high momentum diffusion and low momentum convection). In turbulent flows, however, very high inertial force affects the boundary layer and generates unsteady vortices in the plasma jet.

For further understanding, the Reynolds number $Re$ at a given temperature $T$ was calculated using

$$Re(T) = \frac{4 G_{sc} M P_0}{\pi \eta(T) D M P_0}$$

(2)

where $G_{sc}$ is the gas flow rate ($m^3 s^{-1}$) in standard conditions of temperature ($T_0 = 273 K$) and pressure ($P_0 = 1.013 \times 10^5 Pa$), $M$ is the molar weight ($4.003 \times 10^{-3} kg mol^{-1}$), and $D$ is the hole diameter ($1.000 \times 10^{-3} m$ for our case). The temperature dependent dynamic viscosity $\eta(T)$ of the helium gas was determined in Pa·s by the Sutherland’s formula

$$\eta(T) = \frac{\eta_0}{T_0 + C} \left( \frac{T}{T_0} \right)^{3/2}$$

(3)

where $\eta_0$ is the reference viscosity at $T_0$ and $C$ is the Sutherland’s constant. Using Equation (2) and (3), the transition from laminar to turbulence was observed at $Re \sim 400$ in our helium plasma jet. Although the transition $Re$ is about a factor of 4 lower than the typical transition value ($Re \sim 1760$ for flow inside a cylindrical pipe, i.e., Poiseuille flow), our Reynolds number is consistent with other reports ($Re \sim$ a few hundred) for the flow transition of helium plasma jet in open air. This low Reynolds number flow transition was observed and explained in helium gas jets by the buoyancy effect. According to these reports, the buoyancy effect may be significant for flow transition in the low momentum and momentum dominated helium jet. The buoyancy affects the self-excited flow oscillation and the transition from the laminar to turbulent flow. The length scale of the flow was determined by the buoyancy-induced vortices which were produced in the stream. Therefore, the turbulent jet is shorter than the laminar jet because the turbulent jet produces many vortices when the flow is mixed with ambient air. Thus, we suggest that the buoyancy may play a similar role in our low Reynolds number plasma jet flow transition, and a further study is left as the future work.

Figure 2. (a) Images of the plasma jet. (b) Visible length (- - -) and the Reynolds number (- - -) of the plasma at different helium flow rate.
Plasma Emission Spectra

Another unique feature of the flow transition in our plasma is the change in color of the jet. The color of the laminar jet is blue-green while the turbulent jet is bright violet to the naked eye.

Shown in Figure 3a and b are the emission spectra for laminar flow (1.0 slpm) and turbulent flow (6.0 slpm), respectively. The CN (B2\(^{3}Σ^-\)-X2\(^{1}Σ^+\), violet system) and C2 (A2\(^{3}Π_σ\)-X2\(^{1}Σ^+\), swan system) molecular spectra in the laminar flow plasma are more dominant than those in the turbulent flow plasma, as shown in Figure 3a. In addition, the hydrogen atomic line (H\(_a\), 656.3 nm) and excited fluorine atomic line (F I, 685.6 nm) are clearly seen in Figure 3b for the laminar flow plasma. However, the hydroxyl radical (OH, 306.4 nm) and excited atomic oxygen (O I, 777 nm) lines are distinctly observed at the turbulent flow plasma.

As depicted in Figure 4a, the intensities of the C2 (516.5 nm), H\(_a\), and F I lines normalized by the He I (706.5 nm) line decrease as the flow rate increases from 1.0 to 6.0 slpm. In particular, C2/He I and F I/He I ratios rapidly drop at the flow transition between 2.0 and 3.0 slpm. As a result, the dominant species of the laminar jet are carbon and fluorine, which are produced from the pyrolysis of PTFE. Usually, the pyrolysis of PTFE occurs at 473 K. Moreover, PTFE has high melt viscosity so that laminar jet discharge with PTFE has higher viscosity than that of the pure helium jet.[30] Because the viscous or friction force of helium gas is much larger than the inertial force in laminar flow, fluorine and carbon species flow in parallel layers with no disruption between layers. Thus, oxygen and water molecules from the air do not easily mix with the laminar jet. Figure 4b depicts emission lines of oxygen related species (OH and O I) and N\(_2^+\) diatomic emission line, normalized by the He I line, at various helium flow rates. The OH/He I, O I/He I, and N\(_2^+\)/He I ratios increase only in the turbulent jet. Because of the big inertial force in helium gas at high flow rate, the gas mixes much more rapidly and completely with ambient air. As the collision frequency increases between electrons and heavy particles in the turbulent jet, the energy transfer from electrons to heavy particles also becomes very active.[31]
Plasma Temperature Measurements

The measured rotational temperature ($T_{rot}$) and excitation temperature ($T_{exc}$) of the plasma jet are shown in Figure 5. In order to obtain $T_{rot}$, the OH (306.4 nm) and N$_2$+ (391.4 nm) diatomic line spectra originated from moisture and nitrogen molecules in the ambient air were investigated using the well-known synthetic method.[32,33] As shown in Figure 5, $T_{rot}$ is gradually decreased as the flow rate increases due to convective cooling. Thus, the molecular chain of PTFE was decomposed into several fluorocarbon products such as C$_2$F$_4$, C$_3$F$_6$, C$_4$F$_8$, C, and polymer at laminar flow.[34]

On the other hand, $T_{exc}$, which is known as the minimum value of the electron temperature in atmospheric pressure plasmas,[35] was determined from the Boltzmann plot using He I atomic emission lines (447.1, 501.6, 587.6, 656.0, 667.8, 706.5, and 728.1 nm). As shown in the figure, $T_{exc}$ is above 1800 K for the laminar flow plasmas, which is about 1.5 times higher than the value at the turbulent flow. Similarly to $T_{rot}$, $T_{exc}$ also decreases as the flow rate increases. The drop of $T_{exc}$ becomes significant at the turbulent flow because of the active energy transfer from electrons to heavy particles.

Surface Modification of the Cover Glass

The produced plasma was implemented to treat the surface of a cover glass. During the plasma treatment, the nozzle-to-substrate distance was fixed at 10 mm to minimize the operational variables. The experimental results showed that the water contact angle measured by a contact angle analyzer (SEO Phoenix) indicated a significant change of wettability. Figure 6a–c shows the untreated glass surface, modified glass surface with the laminar jet and the turbulent jet plasma, respectively. Compared to the contact angle of 40° of the untreated cover glass, which was similarly observed previously,[36] the contact angle of the turbulent jet plasma treated surface was reduced to 9°, showing a strong hydrophilic property. The hydrophilicity of the surface was confirmed by the FT-IR attenuated total reflectance (ATR) spectroscopy of the treated surface that showed hydroxyl (O–H) absorption bands in the range of 3 600–3 100 cm$^{-1}$. This result implies that the turbulent jet plasma increases the surface energy by the water-attracting functional groups such as O–H. As opposed to the turbulent jet plasma treated case, the contact angle of the laminar jet plasma treated surface was dramatically increased to 145°, demonstrating strong hydrophobicity and even local super-hydrophobicity (>150°). Upon considering the contact angle of the untreated PTFE surface is 108°, we expect that the PTFE hydrophobic tails (C$_n$F$_{2n+2}$) are covered on the glass by the laminar jet treatment. This dramatic change in the contact angle is understandable by the emission spectra shown in Figure 3. The C–F dominant plasma jet was produced at the laminar flow as opposed to the usual helium plasma produced at the turbulent flow, indicating that this strong hydrophobicity is attributed to these C and F functional groups. These results demonstrate that the surface wettability is changed from hydrophilic to hydrophobic (and vice versa) due to the different chemical species inside the plasma, depending only on the helium flow rate at the same plasma source.

The atomic force microscopy (AFM) demonstrated a substantial change in the roughness of the modified surface, and the result is shown in Figure 7. Even with the rather short plasma treatment time (60 s), the rough-
ness was remarkably changed from 0.888 nm of the untreated glass surface to 200.0 nm by the laminar jet plasma treatment and to 0.240 nm by the turbulent jet plasma treatment, respectively. Instead of utilizing complicated plasma etching techniques that are often employed to increase the roughness of artificial material surfaces, our results demonstrate control of material surface wettability simply by helium gas flow rate of the atmospheric pressure plasma jet. Such results are very promising from an industrial point of view and require further study. In addition, our measurement of the contact angle of the plasma treated sample for 30 days exhibited little change, i.e., 145° to 144° for the hydrophobic treated surface and 9° to 11° for the hydrophilic treated surface, which indicates that the modified surface is very stable.

Conclusion

By only controlling the gas flow rate of the micro jet plasma, the flow transition from laminar to turbulent occurred at a certain gas flow rate. As a result, plasma characteristics including plasma emission lines, dominant reactive species, rotational temperature, and excitation temperature were significantly altered. The unique feature of the plasma in our experiment utilizing a PTFE piece in the discharge region is that C–F species originated from the pyrolysis of PTFE are the dominant reactive species in the laminar flow because of the low density helium and high rotational temperature. In the turbulent jet, however, oxygen and nitrogen related species are dominant as ambient gas species are rapidly mixed with the supplied helium gas. This difference brought about only by the supply gas flow rate can be effectively utilized to control surface wettability. Measurements of water contact angle, AFM, FT-IR, and the optical spectra emitted from the plasma demonstrated that the modifications of the glass surface into strong hydrophobic and strong hydrophilic surfaces were produced by the C–F dominant laminar jet and the He dominant turbulent jet plasma, respectively. In addition, the high stability of the modified surface was confirmed by showing the negligible change in contact angle for more than 30 days.

Keywords: atmospheric pressure glow discharges (APGD); flow transition; plasma polymerization; polytetrafluoroethylene (PTFE); surface modification

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