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Feasibility study of material surface modification by millimeter size plasmas produced in a pin to plane electrode configuration

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Abstract

A few millimeter size plasma was generated in a pin to plane electrode configuration with either Aluminum or Indium Tin Oxide glass. Depending on the plane electrode material, the plasma showed either corona or corona-dielectric barrier discharge hybrid discharge characteristics. From electrical and optical diagnostics, it was found that the hybrid discharge was more electrically stable and had lower rotational temperature. A feasibility study of material surface modification was performed with the hybrid discharge. All samples such as polyethylene and polypropylene films became more hydrophilic, and the surface property was changed only within the radius of less than about 12 mm. In addition, several effects of gas temperature and treatment time on the surface modification were studied besides the durability.

Keywords: Atmospheric plasma; Corona-DBD hybrid plasma; Surface modification

1. Introduction

Plasma treatment is one means of modifying polymer surfaces to improve their adhesion as well as to provide biocompatibility of materials such as polyvinyldifluoride (PVDF), phosphorous glass (SiPOC), and polyvinyl chloride (PVC) [1,2]. Plasmas are attractive for surface modification, because they change surface properties without affecting the favorable bulk characteristics. Also, the plasma surface modification process is usually fast and is a dry process. Thus, the plasma modification of polymer surfaces is becoming more highly utilized [3]. The most general plasma type for the surface modification has been the corona involving dielectric barrier discharges (DBD). The nature of plasma interaction with various polymer surfaces is determined by plasma source configuration and operating parameters, therefore, a proper selection of electrode configuration, power supply design, and supply gas help minimize or even eliminate the filamentary discharges, which often lead to a nonuniform surface treatment, and it also helps generating glow discharges instead.

Considering the discharge regime is an important issue as it can have a significant effect on the surface modification by changing both the ratio of electrons to metastables and the spatial distribution of active species [4]. It was actually shown that wettability of the polypropylene was increased greater by a glow DBD than by a filamentary DBD [5].

On the other hand, there is sometimes a need for a local or small area surface treatment. Therefore, a pin to plane electrode type was chosen in this work to generate a glow discharge of small size. The plane electrode was either an Aluminum conductor or an Indium Tin Oxide (ITO) glass for the study of dielectric effects on the discharge characteristics. Then, a feasibility study for plasma surface modification was performed for various materials, mostly polymers, with the ITO glass plane electrode, which gave better discharge characteristics for the surface modification.

2. Experimental setup

Fig. 1(a) shows the experimental setup with a pin to plane electrode configuration. The copper pin electrode (1) of 360 μm in radius was located in a cylindrical pyrex tube (2) of 3 mm in radius. The plane electrode (3) was either an Aluminum conductor or an ITO glass (thickness of 0.7 mm) that was connected to ground through a 50 Ω shunt resistor (4) to measure current. All experiments were performed at the atmospheric pressure in the ambient air. The chemically 99.99% pure helium gas (5) was

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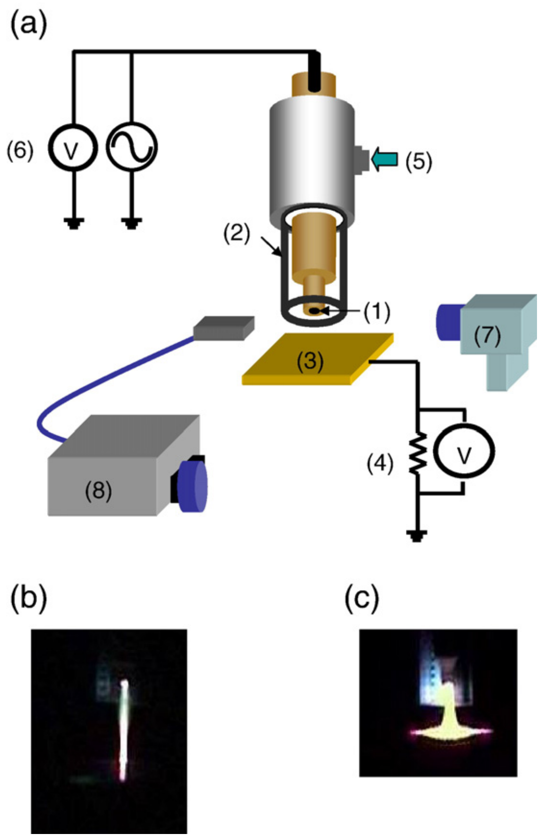

Fig. 1. (a) Experimental setup. Plasma images for a discharge source, consisting of (b) pin to conducting plane electrode and (c) pin to conducting plane electrode with a dielectric barrier.

supplied along the pyrex tube and it reached the pin electrode with a gas flow rate controlled in the range of (5–25) lpm (liters per minute). The AC power source (FT Lab. HPSI 200) (6), which had a controllable input frequency (f_{in}) and voltage (V_{in}) in the range of (20–80) kHz and (0–2000) V, respectively, was connected to the pin electrode. The voltage and current were measured with a digital oscilloscope (Tektronics TDS224). To reduce experimental parameters, the f_{in} and helium gas flow rate were fixed as 50 kHz and 10 lpm, respectively.

A charge coupled device (CCD) (7) camera was used to obtain visual images of the plasma and to measure contact angle of a water drop to study change of the surface wettability before and after the plasma treatment. A Chromex 250is spectrometer (8) was employed to acquire the molecular emission spectrum of the plasma which was then compared to the synthetic spectrum to determine the rotational temperature of the plasma [6].

3. Results and discussions

3.1. Corona versus corona-DBD hybrid discharges

With the experimental setup, the produced plasmas were a conventional corona type with an Aluminum plane electrode and a corona-DBD hybrid type with an ITO glass plane electrode. Apparently, the plasma shapes were different as illustrated in Fig. 1(b) and (c). Firstly, Fig. 1(b) corresponds to the corona type for the inter-electrode distance of 8 mm and the input voltage of 1800 V. At the discharge onset, a glow was seen only near the periphery of the pin electrode, and soon after, a glow was observed near the plane electrode as well. Afterwards, the glows at each electrode grew in both brightness and size until they were connected by a thin cylindrical shape plasma. The typical radius of the plasma was about 360 μm. Secondly, Fig. 1(c) corresponds to the hybrid type for the inter-electrode distance of 5 mm and the input voltage of 2000 V. Replacing the conducting electrode to an electrode with a dielectric (glass) barrier made the plasma more like a cone shape, which was caused by the dielectric charging that is commonly observed in typical DBD's. The typical size of the plasma was about 360 μm in radius at the end of the pin electrode and 3.5 mm in radius at the dielectric surface. However, its size could be varied to some extent by controlling parameters such as the inter-electrode distance and the helium flow rate.

The current and voltage (*I–V*) characteristic curve with power dissipated to the plasma are depicted in Fig. 2(a) for the corona type at the inter-electrode distance of 8 mm and Fig. 2(b) for the hybrid type at the inter-electrode distance of 5 mm, respectively. For the inter-electrode distance less than 5 mm, the corona type discharge was unstable, i.e., the corona to spark transition occurred at the onset or at the very beginning of the discharge.

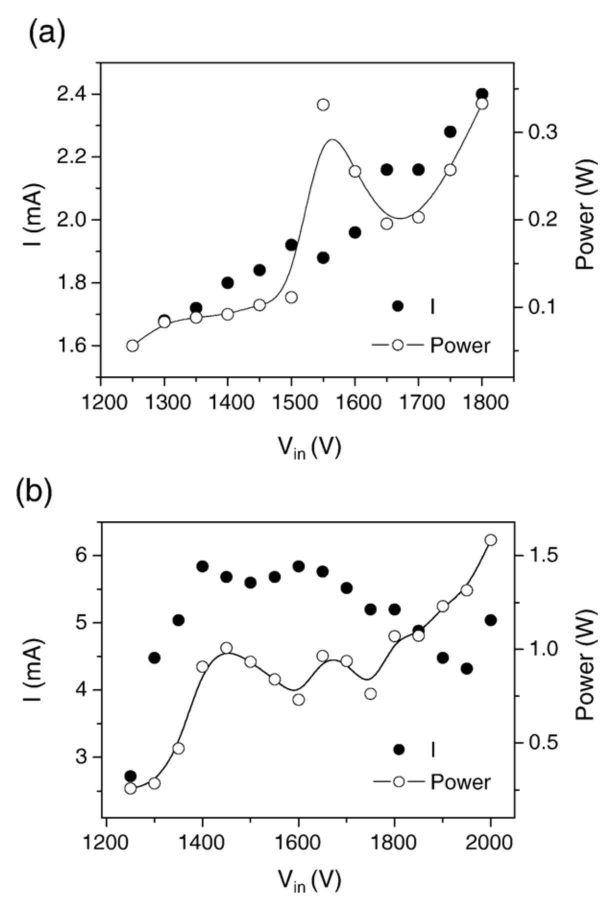

Fig. 2. *I–V* characteristic curve and power dissipated to the plasma for a discharge source consisting of (a) pin to conducting plane electrode and (b) pin to conducting plane electrode with a dielectric barrier.

However, the hybrid type discharge was stable for the inter-electrode distance as small as 3 mm. As shown in Fig. 2, the hybrid type had a higher current, and it still did not become unstable.

The gas temperature (T_{gas}) is an important variable in the atmospheric pressure plasmas in the application point of view, especially for the processes of heavy particles involved. It is closely related to the rotational temperature (T_{rot}) in the atmospheric plasma in which the rotational–translational relaxation is fast enough to equilibrate T_{rot} and T_{gas} [7]. Thus, T_{gas} can be indirectly known by measuring T_{rot}, which was obtained in this study by analyzing the N_2^+ diatomic emission spectra originated from the nitrogen molecules in the ambient air. T_{rot} was measured for both discharge types by varying the input voltage within our power supply limit. The measurement showed that T_{rot} was almost linearly increased with the input voltage for both types as illustrated in Fig. 3. At the low input voltage, T_{rot} was as low as almost the room temperature (∼ 300 K) for both types of the discharges, but the temperature of the corona type was more than 100 K higher than that of the hybrid type at the same input voltage. In these plots, the inter-electrode distance of the hybrid type was shorter (5 mm) than that of the corona type (8 mm), but even when the inter-electrode distance was same as 8 mm for both systems, T_{rot} of the hybrid type was still much lower. More precisely, the maximum temperature, which was limited by the power supply as noted above, of the hybrid type was about 460 K while that of the corona type was about 530 K for the same inter-electrode distance of 8 mm. The reason why T_{rot} of the corona type was measured to be higher than that of the hybrid plasma as shown in Fig. 3, although the power deposited to the corona type plasma was lower (Fig. 2), is due to the smaller volume of the corona type plasma than that of the hybrid type by a factor of ∼ 5. Supposed that the input power was deposited throughout the plasma volume, the estimated power density for the corona type is about 1.7 times larger than that for the hybrid type (0.102 W/mm^3 versus 0.062 W/mm^3 under the same condition of the V_{in} = 1800 V), which brought about the higher T_{rot} for the corona type. The detailed results of the discharge characteristics based on the electrical and optical emission diagnostics will be reported elsewhere.

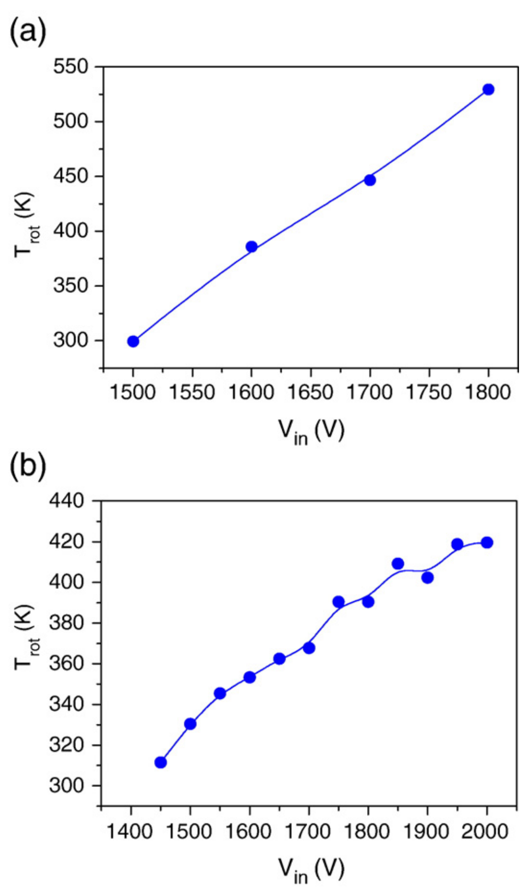

Fig. 3. Rotational temperature against the input voltage for a discharge source consisting of (a) pin to conducting plane electrode and (b) pin to conducting plane electrode with a dielectric barrier.

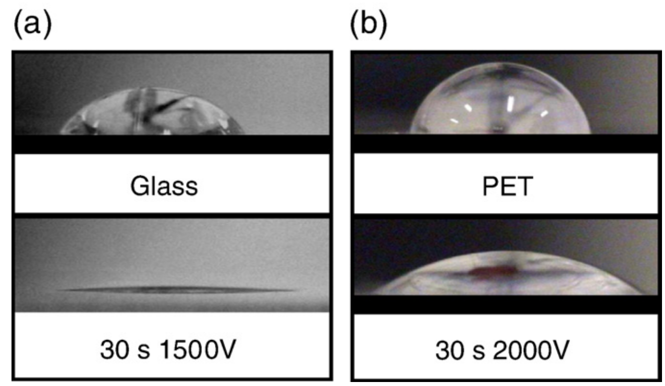

Fig. 4. Images showing the contact angle change for (a) glass and (b) PET before (upper) and after (lower) the plasma treatments for 30 s.

3.2. Feasibility of material surface modification

With the developed corona-DBD hybrid discharge system, a feasibility study of plasma surface modification was performed. Several material samples were treated with the plasma, and the resulting changes of their surface property, especially the wettability, was investigated by the contact angle measurement.

Fig. 4 illustrates samples of glass and PET before and after the plasma treatment. As shown in the pictures, both samples became more hydrophilic after the treatment. In the case of glass, the contact angle was originally 56° and changed to 8° by the plasma treatment for 30 s at the input voltage of 1500 V. On the other hand, the PET first had a contact angle of 77°, which lowered to 34° as well after the 30 s treatment at the input voltage of 2000 V.

Other samples of polyethylene (PE) and polypropylene (PP) were investigated in detail. The samples were films of thickness less than 200 μm, but they could be treated without any thermal damage. The contact angle of the untreated polyethylene and polypropylene films was about 99° and 88°, respectively. Firstly, the two films were treated for 30 s at different input voltages [Fig. 5(a)] to demonstrate the gas temperature effect on the surface modification. As already seen from Fig. 3(b), T_{rot} of the plasma was varied with the input voltage so that 1500 V,

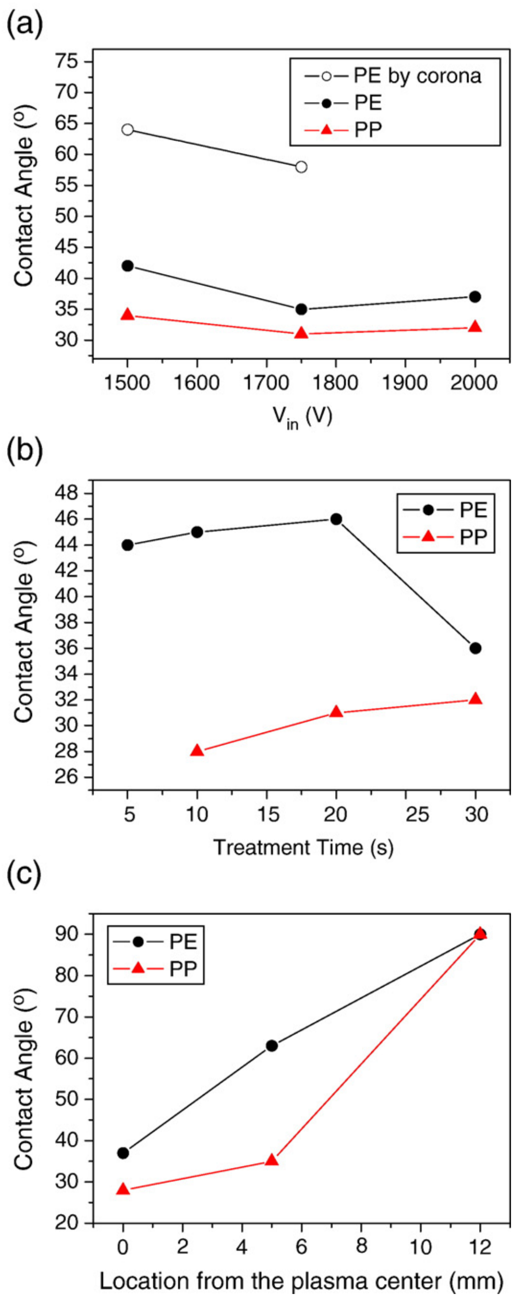

Fig. 5. Contact angle versus (a) input voltage, (b) treatment duration, and (c) treated location from the plasma radial center for polyethylene and polypropylene films.

1750 V, and 2000 V corresponded to 330 K, 390 K, and 420 K, respectively. The results showed that both kinds of films exhibited similar patterns against the input voltage changes, and the contact angle of both films was smallest when they were treated at the input voltage of 1750 V or equivalently at the rotational temperature of 390 K. In addition, in order to make sure the superiority of the hybrid type over the corona type for the wettability enhancement, the polyethylene film was treated by the corona type discharge as well. As depicted in Fig. 5(a), the contact angle of the polyethylene film treated by the corona type plasma was more than 20° larger than that treated by the hybrid type plasma. Once again, it was proved that the hybrid type was more appropriate for the surface treatment than the corona type. Secondly, the films were treated at the fixed input voltage of 2000 V for different treatment duration [Fig. 5(b)]. In the case of the polyethylene film, the contact angle did not vary much between the treatment duration of 5 s and 20 s, but it was reduced significantly for the treatment duration of 30 s. On the contrary, the contact angle of the polypropylene film was smaller when the treatment duration was 10 s and then somewhat saturated for longer treatment duration. Finally, in order to confirm the purpose of small plasma surface treatment, the contact angle was measured at a few points apart from the radial plasma center where the plasma was in direct contact with the sample. As shown in Fig. 5(c), the contact angle increased as the measuring location became more distant from the plasma radial center point. When it was about 12 mm away from the center point, the contact angle was almost same as those of untreated samples.

Furthermore, the contact angle was measured as time passed by to determine the aging time for checking the durability of the modified surface. Fig. 6(a) shows that although the contact angle of the polyethylene film was increased from 37° to 67° just 30 min after the end of plasma exposure, it remained so for more than 30 h. In addition, the dependence of the durability on the input voltage was also investigated by measuring the contact angle 1 week after the plasma treatment. As illustrated in Fig. 6

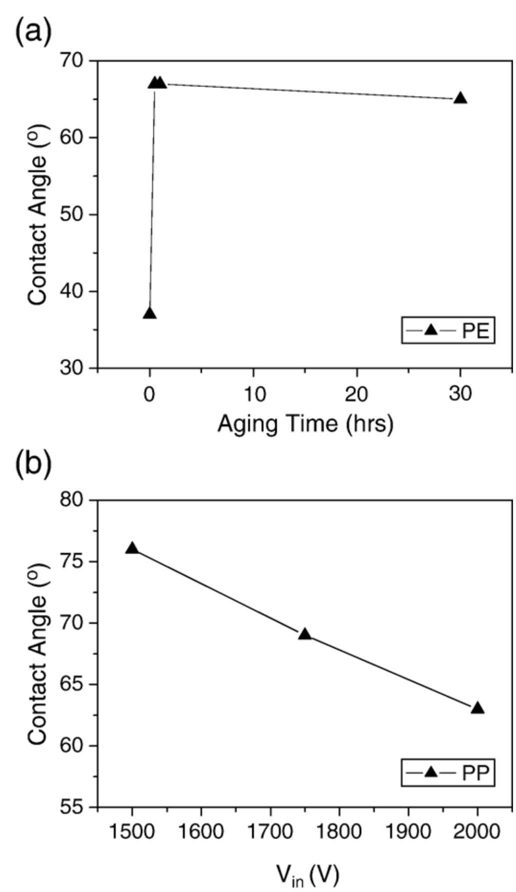

Fig. 6. (a) Change of the contact angle against the aging time for a polyethylene film. (b) Input voltage effects on the aging time for a polypropylene film 1 week after the plasma treatment.

(b), the contact angle of the polypropylene film was increased less, i.e., restored less when the input voltage was higher or at higher T_{rot}.

4. Conclusions

A few millimeter size plasma source was generated in a pin to plane electrode configuration with a copper pin electrode and a conducting plane electrode with and without a dielectric barrier. The generated plasmas showed differences: First, the plasma shape of the corona-DBD hybrid type was cone-shaped while that of the corona type was thin cylindrical. The plasma size of the hybrid type could be varied while that of the corona type was almost invariant. Second, the hybrid type was more electrically stable than the corona type, or specifically, no transition to a spark occurred at the inter-electrode distance less than 5 mm while the corona type became a spark soon after the discharge onset at the inter-electrode distance of 5 mm. Third, the hybrid type demonstrated a lower rotational temperature than the corona type. For instance, its rotational temperature was about 70 K smaller than the corona type under the same operational condition.

Since the hybrid type plasma showed more stable operation with a lower rotational temperature, besides the cone shape larger plasma at the plane electrode, it was employed for a feasibility study of the material surface modification. In order to make sure that the hybrid type is more appropriate for the surface treatment, the same sample of polyethylene was treated by both plasma types, and it was confirmed that the hybrid plasma treatment resulted in a greater wettability than the corona plasma treatment. Then, all samples of glass, PET, polyethylene, and polypropylene were treated with the hybrid plasma, which resulted in becoming more hydrophilic than before the treatment. It was found that there was an optimum condition for the rotational temperature and the treatment duration which resulted in the minimum contact angle. On the other hand, it was confirmed that the hybrid type was suitable for the local or small area surface treatment as the surface property was changed only within the radius of less than about 12 mm. In addition, the aging test of the modified surface indicated that a higher gas temperature had a better durability which lasted more than a week.

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