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Surface Modification of Polyethylene in Dielectric Barrier Discharge (DBD) Plasma Under Atmospheric-Pressure

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***Abstract* – In this paper, the surface treatment method using a dielectric barrier discharge (DBD) of damped oscillation type pulse was discussed. The effects of the discharge parameters such as peak voltage, gas combinations, treatment time, the distance between electrodes, etc., on plasma characteristics were studied. Furthermore, the spectrum of some radicals from DBD discharge plasma was measured by spectra analysis instrument. The hydrophilicity of PE film treated under various discharge conditions was studied.**

***Keywords* – Surface Modification, DBD, Contact Angle, Thin Film, Plasma Treatment.**

I. Introduction

In general, various plasmas are used for thin film deposition and treatment. Dielectric battier discharge (DBD), glow discharge (GD) and corona discharge (CD) can generate plasmas at atmospheric pressures, eliminating the expensive vacuum equipment and measurement tools. The energy level of electrons in plasma discharge is high enough (0.5–20 eV) to generate different active species and to dissociate most of the chemical bonds in organic compounds. Hence it has been widely used in chemical processing such as chemical vaporous deposition or surface modification via plasma polymerization and etching [1–6]. These chemical processes with non-thermal discharge plasmas becomes increasingly critical in various materials processing technologies [1-3, 7]. Especially, the dielectric barrier discharge offers one of the most effective non-thermal plasma sources in the atmospheric pressure, due to its features of large plasma area. DBD discharge, known as micro-streamer discharge at atmospheric pressure, is characterized by the effective conversion of the applied electric field to chemical and physical effects in gases, and thereby to the modification of material surfaces. DBD Plasma technology is an attractive approach for surface modifications, and some efforts of applying this technology to the surface treatment of film have been reported [7–16]. Advantages of DBD have made it possible to treat polymer material surfaces rapidly, continuously and uniformly under atmospheric pressure. Non-thermal plasma resulted from DBD generates abundant excited species, free radicals and ions, which leads to the reactions of a few nanometers on surface of the film and results in chemical and physical changes [7, 14]. Compared with the common DBD with 50Hz AC power source, DBD with high frequency pulse voltage can avoid the local overheat of micro-discharges, and improve discharge efficiency under certain conditions [4, 7].

A variety of polymers have been treated by discharge plasmas, including polyimide [17, 18], polypropylene (PP) [3], polyethylene (PE) [2, 3], polystyrene [15], polycarbonate [19, 20]. The primal goal of plasma treatments is generally to improve the wetting and adhesion properties of the polymers. The atmospheric pressure plasma treatment of low density polyethylene and polyterephthalate improved adhesion by factors of two to ten have been studied [1, 21].

Plasma surface treatment of polymers primarily results in the oxidation of the surface by the generation of functional groups such as C–OH (alcohol), C–O–O–H (hydroperoxide), H–C=O (aldehyde), C=O (carbonyl), C–O–C=O (ester), C–O–O• (peroxy), H–O–C=O (acid), OC(O)O (carbonate), and NH_2 (amine)[1]. Foerch and Hare et al [22, 23] used an air plasma to treat PE and observed the formation of ester, alcohol, carbonyl, and acid groups by x-ray photoelectron spectroscopy. Tsutsui et al. [24] investigated surface modifications of pigments using a rotary plasma reactor and reported that oxygen plasma was suitable for the generation of acidic groups on pigment surfaces, while NH_3 plasma was good for the generation of basic groups.

In this paper, the effects of the discharge parameters such as peak voltage, gas combinations, treatment time, the distance between electrodes, etc., on plasma characteristics and film surface modifications were studied. The spectrum of some radicals from DBD discharge plasma was measured by spectra analysis instrument, the characteristics of contact angle and discharge conditions were studied.

II. Experimental Setup and Methods

A. Experimental Setup

A schematic diagram of the experimental arrangement is shown in Fig. 1. High voltage pulse power source can produce 1-12kV peak voltage. Pulse repetition frequency varied from 50Hz to10 kHz and was controlled by modulator. The DBD reactor consist of between two rectangular plane-parallel aluminum electrodes with 5 x5cm, and both the electrodes were covered by quiz glass planes with thickness 3 mm. The discharge current and voltages were measured by Digital Storage Oscilloscope (TDS 2024 B). The wide bandwidth voltage and current probes were used to monitor the electrical parameters of the DBD circuit. The voltage and current waveforms of the discharge system were recorded by the voltage probe (Voltage probe, Tektronix P6015) and current probe (Current probe, Pearson Electronics 6219). Furthermore, the emission spectrum in discharge system were measured by Photonic multi-channel spectral analyzer, Optical emission spectroscopy was used to detect plasma species such as OH, O, N and O_2 and to characterize the plasma in the atmospheric pressure as a function of discharge parameters.

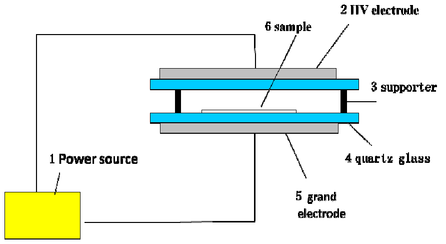


Fig. 1. Experimental setup of treatment polymer with DBD

B. Materials Preparation

The material to be treated was a commercial PE film with a thickness of 0.075mm and rectangle of 40 mm × 40 mm. All untreated samples were rinsed with alcohol for 10 minutes, and then cleaned with deionized water using an ultrasonic cleaner. Finally the samples were dried before plasma treatment. Thin film samples were placed on the lower quartz glass plane covering the grounded planar aluminum electrodes. For all those experiments, plasma treatments were performed in air at atmospheric pressure and room temperature.

III. Results and Discussion

A. Discharge Characteristics

Figure 2 shows the typical discharge of current and voltage waveforms. The voltage is pulse voltage of damped oscillation with 5kHz main frequency and frequency of damped oscillation is about 16kHz. When the pulse voltage is applied to reactor, the current of 10 µs long duration was observed at main pulse voltage. This peak current is like uniform glow discharge. Many micro-current peaks were found at damped pulse voltage. These current pulses show that a lot of micro streamer discharge occurs in the reactor.

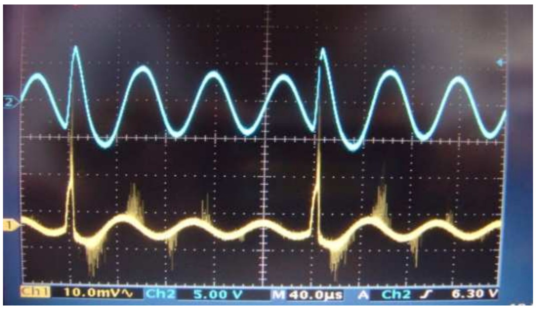


Fig. 2. Typical voltage and current waveforms of DBD (above : voltage, Bottom : current)

The discharge images of DBD reactor is shown in figure 3, it is combination of like glow discharge and micro-streamer discharge. It is considered for uniform discharge for thin film treatment due to the time integral effect of several ten seconds for treatment time.

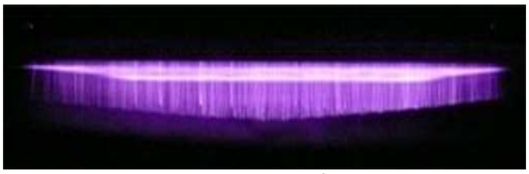


Fig. 3. The discharge images of DBD reactor, 2mm discharge gap

B. Emission Spectrum of DBD Plasma in Atmospheric Air

The emission spectrum of DBD plasma in atmospheric air is shown in Fig.4, several strong emission peaks were observed between 300 to 450nm wavelength. It is found that the strong peaks belong to the transitions of N_2 second positive system and the weak peaks belong to the transitions of N_2^+ First Negative System, after comparison and confirmation with literature [25]. The transitions of N_2 second positive system correspond to states of $C^3\prod_u \rightarrow B^3\prod_g$, the wavelength of bank is 337.nm. The transitions of N_2^+ First Negative System correspond to states of $B^2\sum^+_u \rightarrow X^2\sum^+_g$, the wavelength of bank are 391.4 and 426.8nm, its intensity is weaker than N_2 intensity. This shows that there are N_2^+ production in discharge system.

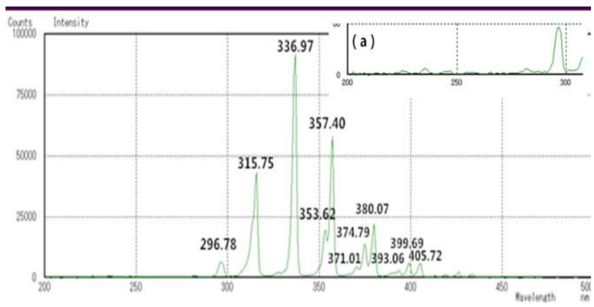
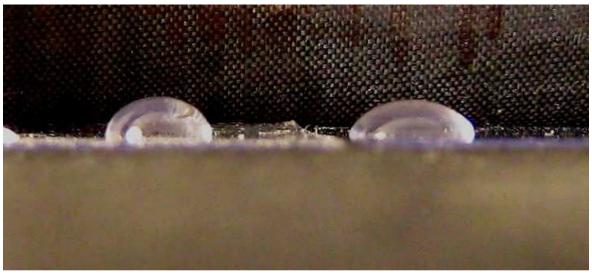


Fig. 4. Emission spectra of air plasma by DBD at atmospheric pressure

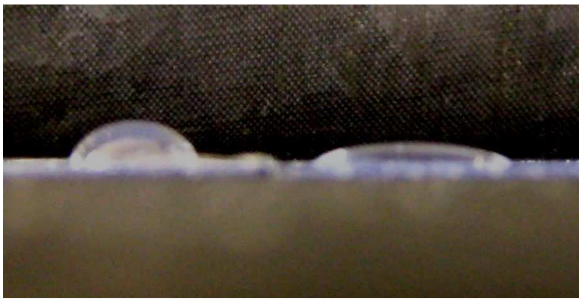
C. Surface Modification of Polyethylene Film with DBD Plasma

The Fig. 5 shows the effect of peak voltage on hydrophilicity of thin film, the treatment time of thin film is 5 seconds and frequency is 5000Hz. The dielectric gas is atmospheric pressure air. The left of Fig.5 is untreated samples, the right are treated samples with 5.4 and 8.1kV, respectively. Clearly, the hydrophilicity of thin film changed with discharge peak voltage.

The contact angle of film decrease with increasing of peak voltage, the contact angle change small when peak voltage is low and change large when peak voltage is than 6kV. The contact angle of untreated film sample is 81°and the contact angle is 31°at treatment voltage of 8.1kV. The contact angle decreased 50° in maximum. This is considered to be the reason that the plasma density is higher when the peak voltage increases leading to more active species of the plasma for more significant surface reaction.



Untreated Sample 5.4kV



Untreated Sample 8.1kV

Fig. 5. The change of hydrophilicity of thin film for different peak voltage

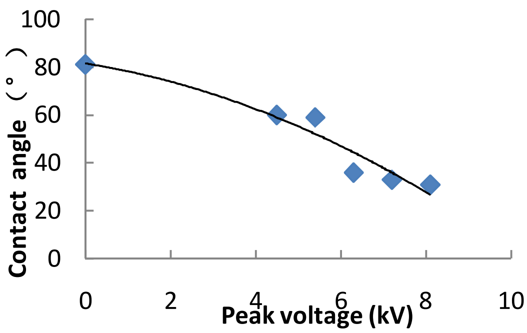


Fig. 6. Effect of discharge voltage on contact angle of film

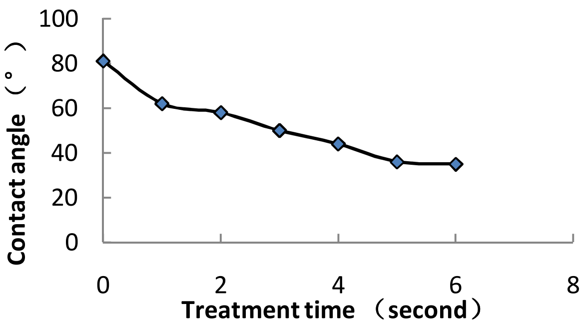


Fig. 7. Effect of treatment time on contact angle of film

As shown in figure 7, from whole tendency, the contact angle decreases with increasing of treatment time, it is that the hydrophilicity of thin film increased. The hydrophilicity of thin film little changed after treatment time is more than 5seconds, the result shows that the cross-linking and etching effect reached dynamic balance at the moment.

Table 1. The chemical bond energy of polymer (eV)

C−H	C−N	C−Cl	C−F
4.3	2.9	3.4	4.4
C=O	C−C	C=C	C≡C
8.0	3.4	6.1	8.4

As mentioned above, the energy level of electrons in plasma discharge is at 0.5–20 eV, the ion energy is about 0-2eV、the metastable state is 0-20eV, and the photons energy of ultraviolet light is about 3-15eV. Most of them are more than chemical bond of polymer material (as shown in Table 1). It can lead to breakdown various chemical bond and to recombine reaction on the polymer surface. In the air plasma, N_2 and O_2 inorganic gases can produce a lot of N, N^+ O, O_2^- radicals, leading to the generation of functional oxygen containing groups on the polymer surface such as C–OH (alcohol), C–O–O–H (hydroperoxide), H–C=O (aldehyde), C=O (carbonyl), C–O–C=O (ester), C–O–O• (peroxy), H–O–C=O (acid), OC(O)O (carbonate), and NH_2 (amine). The surface oxygen concentration increases with increasing of plasma density and then plateaus [4]. The formation of these chemical oxygen containing groups realized the modification of film surface.

IV. Conclusions

In this experiment, the basic characteristics of dielectric barrier discharges with pulse voltage discharges operated at the atmospheric pressure were investigated by a high voltage and current probe and optical emission spectrum of plasma was studied. Also, using some of the stable DBD pulse discharge, the characteristics of organic thin film hydrophilicity and contact angles were investigated. Our results show that

1. The DBD discharge droved by damped pulse oscillation shows combination of like glow discharge and micro-streamer discharge.
2. Through measurement of optical emission spectrum of DBD, there are N_2^+, N and, O in the plasma, their intensities appear to increase with the increase of peak voltage.
3. The surface hydrophilicity of organic thin film could effectively improved by the DBD plasma treatment.
4. The contact angles of PE thin film decreased with the increase of peak voltage and treatment time, and plateaus at some value.

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