HYDROPHOBIC MODIFICATION OF POLYETHYLENE TEREPHTHALATE SURFACE USING NANOSECOND-PULSE DBD AT ATMOSPHERIC PRESSURE

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ABSTRACT

Compared with the traditional method for surface treatment, non-thermal plasmas have advantages such as low pollution, simple process and low cost. In the paper, non-thermal plasmas are generated by dielectric barrier discharge (DBD) excited by home-made nanosecond-pulse generator with a rise time of ~70 ns and a full with at half maximum of ~100ns. Such plasmas are used to modify the hydrophobicity of the surface of polyethylene terephthalate (PET) in atmospheric carbon tetrafluoride (CF_4). The static water contact angle of the PET surface is measured before and after the treatments. The effects of the flow rate of CF_4, treatment time and CF_4 ratio in the CF_4/N_2 mixture on the surface treatment are presented. Experimental results show that the hydrophobicity of the PET surface can be enhanced after DBD plasma treatment in CF_4. The static water contact angle of the PET surface can increase from 68° to 100°.

1. INTRODUCTION

Polymer materials have been extensively used for various industrial applications, for example, polyethylene terephthalate (PET) is one kind of widely used material in the fields such as electrical engineering, medical equipment, packaging and automobile industries due to its good mechanical and chemical properties, easy processing and low cost [1]. However, in some applications, the PET surface needs to meet hydrophobic requirement for preventing snow, pollution, antioxidant and current conduction. Therefore, treatment of the PET surface is necessary for its wide use[2].

Nanosecond-pulse dielectric barrier discharge (DBD) can provide non-thermal plasmas with extremely high energy and high density, which could set off a series of complicated physical and chemical reactions in the surface treatment of polymers. Moreover, it could provide extremely high peak power for the excitation of gas discharges with fast rise time and high overvoltage to prevent the transition from homogeneous DBD to filamentary DBD at atmospheric pressure [3-4].Our previous work presented investigations on surface treatment of PET and polyimide films using nanosecond-pulse DBD [3-4]. Results showed that nanosecond-pulse DBD consumed less power density but performed better hydrophilicity effect than AC DBD. In addition, hydrophobic coating was formed on the polymethylmethacrylate (PMMA) surface by a nanosecond-pulse DBD. The PMMA surface was covered with silicone oil before the DBD treatment, and after the treatment in air, the contact angle of the surface was increased to 92° from 72 ° [5].In this paper, hydrophobic treatment on PET surface is conducted by nanosecond-pulse DBD in CF_4.

2. EXPERIMENTAL SET-UP AND MATERIAL

The diagram of the experimental arrangement is shown in Fig. 1. In the experiments, a one-stage magnetic compression pulsed generator was used to produce repetitive pulses [5]. The output pulses had an amplitude up to ~ 40 kV, a rise time of ~70 ns and a full width at half maximum (FWHM) of ~100 ns. The pulse repetition frequency (PRF) of the generators varied from 1 Hz to 1000 Hz and was controlled by a trigger modulator. The DBD was created between two circular plane-parallel aluminum

electrodes with a diameter of 50 mm. The electrodes were covered by two glass plates with a thickness of 2 mm. The gap spacing was 2 mm. The DBD device was placed in a vacuum chamber, which was a cylinder glass chamber covered with two stainless steel caps. The chamber was pumped by a rotary-vane vacuum pump (2XZ-4, Kangjia Ltd, Shanghai, China), and its vacuum degree was down to 5 Pa. CF_4 was used as media gas and the gas flow rate was controlled by a mass flow meter division (D08-4F, Beijing Sevenstar Electronics, China).

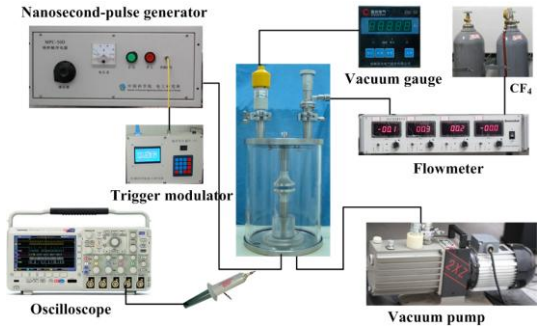

Fig. 1 Schematic view of the DBD set-up for surface treatment

Wide bandwidth voltage and current probes were used to monitor the electrical parameters of the DBD circuit. Voltage was measured by a high-voltage probe (Tektronix, P6015, 1000:1).Current was measured by a current probe (Pearson, Model 4100, 1 V/A). A oscilloscope (Tektronix DPO2024, with a bandwidth of 200 MHz and a time resolution of 1 GS/s) was used to record the electrical signals. The vacuum degree was measured by a resistance vacuum gauge (ZDZ-52T, Chengdu Electric Technology Co., Ltd., China).

The materials for the treatment are commercial PET with a thickness of 0.2 mm and an area of 5 × 5 cm^2. For the DBD processing, the samples were placed on the glass layer covering the grounded planar aluminum electrodes. All samples were first rinsed with acetone and alcohol, then cleaned with deionized water by an ultrasonic cleaner, and finally dried in a vacuum drying box for 1 hour before the plasma treatment. For all these experiments, plasma treatments were operated in CF_4 at atmospheric pressure and room temperature. In order to evaluate the effect of the plasma treatment, contact angle is measured. The values of contact angle shown in this paper are the average of 8 measured values.

3. EXPERIMENTAL RESULTS

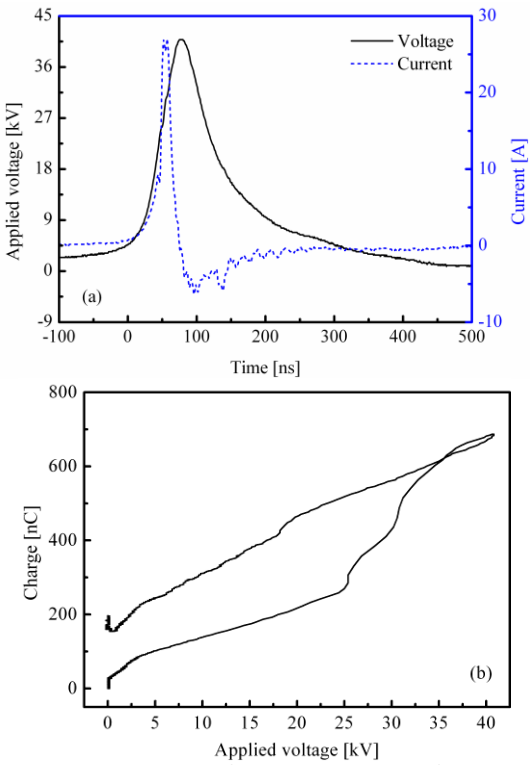

Fig.. 2 Voltage-current waveform and Lissajous plot for treatment: (a) voltage-current waveforms for treatment; (b) Lissajous plot.

Before the treatment, the chamber was first pumped down to 5 Pa, and then high-purity CF_4 was filled into it until the pressure reached the atmospheric pressure. Fig. 2 shows typical voltage-current waveforms and Lissajous plot. The experimental conditions were as follows: the applied voltage was 40 kV, the PRF was 500 Hz and the flow rate of CF_4 was 3 L/min. It could be seen that the amplitude of the current was 25 A. Moreover, a negative current with an amplitude of 5 A was observed during the fall-time of the applied voltage. Fig. 2(b) shows the Lissajous plot of the DBD. In Lissajous plot, the charge was the time integrated current. On the basis of the area of the Lissajous plot, the energy deposition per pulse could be calculated and it was 5.6 mJ. Under the condition that the PRF was 500 Hz, the power consumed per pulse was calculated to be 2.8 W. In addition, the area of the electrode in the experiments was 19.6 cm^2, so the power density was calculate to be 142.8 mW/cm^2. Note that the power density was smaller than that in DBD excited by AC power supplies.

The effect of several parameters influencing the DBD treatment is investigated. Water contact angle of the PET surface as a function of the CF_4 flow is shown in Fig. 3. The experimental

conditions were as follows: the applied voltage was 40 kV, the PRF was 500 Hz, and treatment time was 300 s. It can be found that the contact angles were smaller than the original value (68°) when the flow rates were 1 L/min and 2 L/min, which indicated a hydrophilic PET surface was obtained. However, when the flow rate increased to 3 L/min, the contact angle was approximately 100°, which indicated a hydrophobic surface was obtained. Further increase of the flow rate could no longer increase the contact angle. Such change of contact angle could be attributed to the relationship of the amount of the fluorine-containing function groups to the CF_4 flow rate. When the flow rate was small, there were only a few of fluorine-containing function groups on the PET surface [6]. Under such condition, the increase of the roughness of PET surface due to etching could further enhance the hydrophilicity of the surface, resulting the decrease of the contact angle. When the flow rate increased to 3 L/min, there were a lot of fluorine-containing function groups on the PET surface, leading to the formation of a hydrophobic coating on the PET surface. Under this condition, increasing the roughness of PET surface could further enhance the hydrophobicity of the surface, resulting in the increase of the contact angle. Furthermore, because the amount of function groups on the PET surface had a limitation, further increase of the CF_4 flow would not enhance the hydrophobic effect.

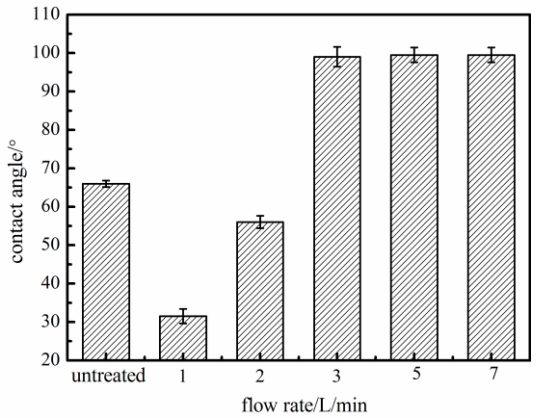

Fig. 3 Water contact angle as a function of the CF4 flow

Fig. 4 shows water contact angle of the PET surface as a function of treatment time. The experimental conditions were as follows: the applied voltage was 40 kV, the PRF was 500 Hz, and the flow rate was 3 L/min. It could be seen that the contact angle was decreased when the treatment time was 100 s. It increased during the next 100 s, however, it was still less than the original value when the treatment time was 200 s. Further increased the treatment time, the contact angle could increase to the maximum of 100°. The change of the contact angle with the treatment time, in our opinion, was also related to the amount of fluorine-containing function groups under different treatment times.

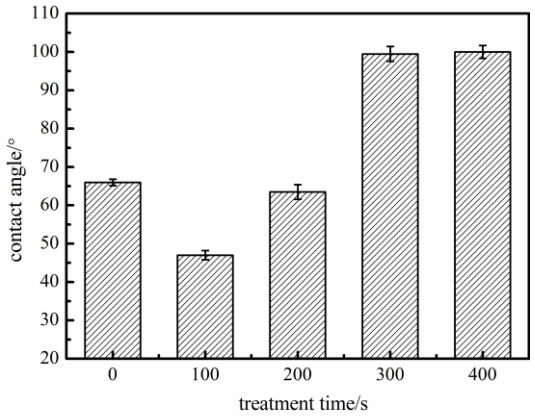

Fig. 4 Water contact angle as a function of the treatment time.

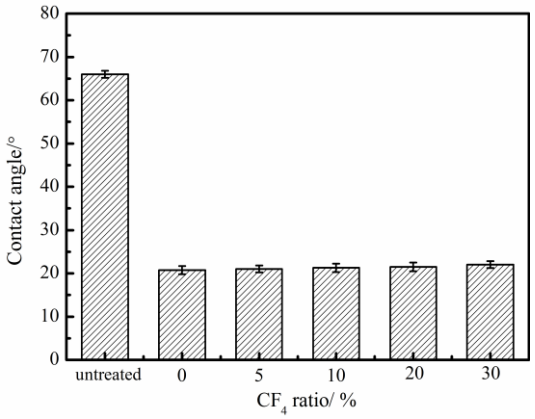

Fig. 5 Water contact angle as a function of the CF4 ratio in CF_4/N_2 mixture

In the experiments, the CF_4/N_2 mixture was used for treatment, and the effect of the CF_4 ratio was shown in Figure 5. It could be observed that as the ratio rose from 0% to 30%, the contact angles were smaller than the original value in all cases, which indicated there was no hydrophobic coating formed on the PET surface. This may be because there were more nitrogen-containing function groups compared to the fluorine-containing ones on the PET surface after the treatment [7]. Nitrogen-containing function groups had strong hydrophilic properties, so the hydrophilicity of the PET surface was enhanced.

According to the different effects of the different parameters mentioned above on the treatment result, the optimal experimental conditions under which the most hydrophobic

coating could be obtained were as follows: the applied voltage was 40 kV, the PRF was 500 Hz, the flow rate was 3 L/min and the treatment time was 300 s. In this case, the water contact angle of the untreated PET surface, which was 68°, could rise to 100° after the DBD treatment in CF_4. The corresponding images of the contact angle of PET surface before and after the treatment was shown in Fig.6.

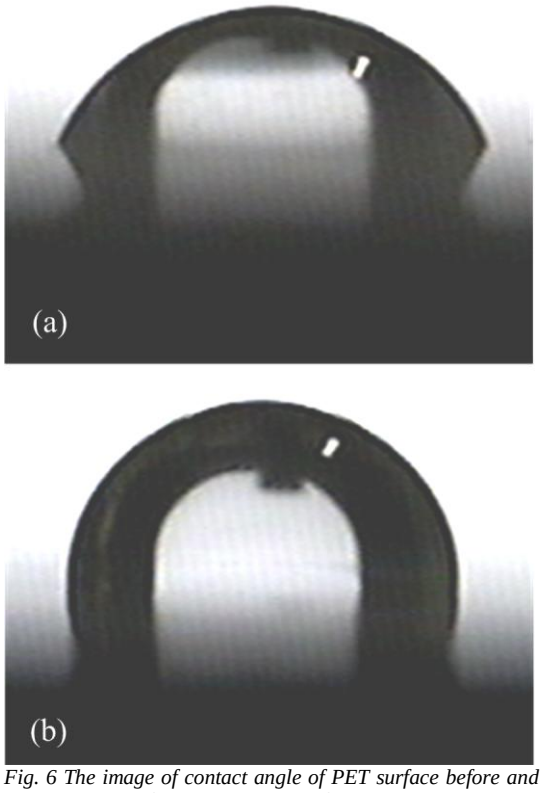

Fig. 6 The image of contact angle of PET surface before and after treatment. (a) before treatment; (b) after treatment

4. CONCLUSION

Surface treatment of PET material using nanosecond-pulse DBD in CF_4 at atmospheric pressure is investigated in this paper. Four conclusions can be drawn from our researches:

a) Water contact of angle could increase from 68° to 100° (the maximum) after the treatment.

b) When the CF_4 flow was less than 3 L/min, the hydrophilicity of PET surface was enhanced, or a hydrophobic coating was formed.

c) When the treatment time was shorter than 300 s, the hydrophilicity of PET surface was enhanced, after that, a hydrophobic coating was formed.

d) When the CF_4 ratio in the CF_4/N_2 mixture was not more than 30%, hydrophilic effect could be enhanced in all cases.

ACKNOWLEDGEMENT

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