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Surface modification of polyimide films using unipolar nanosecond-pulse DBD in atmospheric air

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ABSTRACT

DBD-induced surface modification is very versatile to increase the adhesion or hydrophilicity of polymer films. In this paper, the DBD is produced by repetitive unipolar nanosecond pulses with a rise time of 15 ns and a full width at half maximum of about 30 ns. The power densities of the homogeneous and filamentary DBDs during plasma treatment are 158 and 192 mW/m^2, respectively, which are significantly less than that using ac DBD processing, and the corresponding plasma dose is also mild compared to AC DBD treatment. Surface treatment of polyimide films using the homogeneous and filamentary DBDs is studied and compared. The change of chemical and physical modification of the surface before and after plasma processing has been evaluated. It can be found that both surface morphology and chemical composition are modified, and the modification includes the rise of hydrophilicity, surface oxidation and the enhancement of surface roughness. Furthermore, the homogeneous DBD is more effective for surface processing than the filamentary DBD, which can be attributed to the fact that the homogeneous DBD can modify the surface more uniformly and introduce more polar functional groups.

1. Introduction

Polymer materials have been extensively used for various industrial applications, for example, polyimide (PI) has been applied to act as substrate material in flexible electronic technology because it has excellent characteristics of high tensile strength, good thermal stability and chemical resistance [1,2]. In order to enhance the adhesion between PI and metal films, surface modification is accordingly required. Compared with other methods such as chemical technique, electrochemical process, and photo-irradiation and so on, the treatment using large-volume non-thermal plasma produced by dielectric barrier discharge (DBD) is an economic, reliable and convenient method [4–6].

Advances in the use of atmospheric pressure discharges, particularly such as DBD, have made it possible to treat polymer surfaces rapidly, continuously and uniformly without using vacuum equipment. Surface modification of polymer films using DBD has been reported by some researchers [7–16], and the adhesion or hydrophilicity properties have been dramatically improved. Non-thermal plasma resulted from DBD generates abundant excited species, free radicals and ions, which leads to the reactions with the first few nanometers of the film and results in chemical and physical changes [14]. In most cases, DBD is driven by an AC power source of 50 Hz or kHz of periodic sine or square waves [7–23]. DBD often works on a filament mode via many streamer micro-discharges, which would result in inhomogeneous treatment and partial thermal degradation of the treated films [18–20]. From a practical point of view, homogeneous discharge at atmospheric pressure is a very desirable condition. However, DBD treatment in the homogeneous mode requires special arrangements [7,17]. Compared with the common DBD using AC power source, DBD using unipolar pulse voltage can avoid the local overheat of micro-discharges, and improve discharge efficiency under certain conditions [24–33]. In our previous papers [34–36], it is found that electrical characteristics of the DBD excited by repetitive unipolar nanosecond pulses are different from that reported ever, such as discharge voltage and current across air gap behaves bipolar pulses and the peak of discharge current can be on an order of hundreds of amperes. In the present work, considering the potential predominance of DBD treatment using repetitive nanosecond-pulse power source, surface modification by the filamentary and homogeneous DBDs is achieved in atmospheric air. The effect of the DBD plasma treatment on surface property and adhesion characteristic of PI films is evaluated by means of water contact angle measurement, scanning electron microscopy (SEM),

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atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Material

The material to be treated was a commercial PI film with a thickness of 0.075 ± 5 mm and an area of 40 mm $\times$ 40 mm. All samples were rinsed first with alcohol, and then cleaned with deionized water using an ultrasonic cleaner, finally dried in vacuum drying setup before plasma treatment. PI samples were placed on the lower glass plane covering the grounded planar aluminum electrodes. For all these experiments, plasma treatments were performed in air at atmospheric pressure and room temperature.

2.2. Experimental setup for DBD treatment

A schematic diagram of the experimental arrangement is shown in Fig. 1. A solid-state pulse generator was used to produce repetitive nanosecond pulses in the treatments [34–36]. Output high voltage pulse of the generator has a rise time of about 15 ns and a full width at half maximum of 20–30 ns. Pulse repetition frequency varied from single shot to 2 kHz and was controlled by a trigger modulator. The generator was an inductive energy storage type, and output voltage was changed by cycled saltwater solution via a parallel connection with the DBD treatment reactor. Plasma treatment was conducted by fixing applied voltage at about 50 kV and pulse repetition frequency at 250 Hz. The DBD was created between two circular plane-parallel aluminum electrodes with a diameter of 7 cm, and both the electrodes were covered by glass planes with different thickness between 1 mm and 4 mm, and an area of 100 mm $\times$ 100 mm.

Similar to the measurement described in [34,35], wide bandwidth voltage and current probes were used to monitor the electrical parameters of the DBD circuit. The voltage probe was a capacitive voltage divider connected to the high-voltage output of SPG200N. The current probe was a current diverter made of a coaxial tubular high-frequency resistor shunt. A Lecroy oscilloscope (WR204Xi, with a bandwidth of 2 GHz and a time resolution of 10 GS/s) was used to record the electrical signals. In addition, discharge images were recorded by a commercial digital camera SONY DSC-H9, which has an exposure time of 0.5 s.

2.3. Measurement for surface analysis

In view of the measurement requirement of surface analysis, contact angle of water, SEM, AFM, and XPS were used in surface analysis.

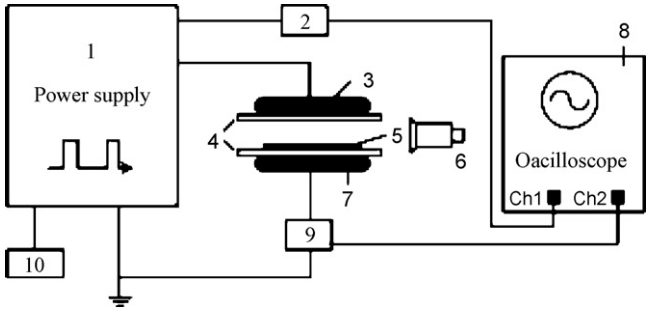

Fig. 1. Schematic view of the DBD set-up used for surface modification (1, repetitive nanosecond-pulse power supply; 2, capacitive voltage divider; 3, upper aluminum electrode; 4, glass planes; 5, PI films; 6, digital camera; 7, lower aluminum electrode; 8, Lecroy WR204Xi oscilloscope; 9, current viewing resistor; 10, trigger modulator).

Static contact angle measurement was made immediately after DBD treatment by dropping 2 μl distilled water on the PI surface. The values of static contact angle were obtained using Laplace–Young curve fitting based on the imaged water drop profile and were the average of eight measured data on different locations.

Surface morphology was investigated by two methods. Firstly, a SEM (JEOL JSM-6701F) observation was used, and the film samples were sputtered and coated with a thin layer of gold on the surface before analysis. Furthermore, an AFM (Digital Instrument D3100) image in tapping mode was performed as a high-resolution method to determine topography and roughness, and the corresponding analysis was done using Nanoscope software.

In order to investigate surface chemical characterization, an XPS (VG Scientific ESCALab220i-XL) analysis was carried out on PI surface. The analysis used nonmonochromatic Mg Kα radiation operating at 300 W and the pressure in the analyzing chamber was maintained at 3×10^{-9} mbar. All XPS-peaks were referred to the C 1s signal at a binding energy of approximately 285 eV [10], and curve fitting of the C 1s peak was done using XPSpeak 4.1 software.

3. Results

3.1. Optical and electrical characterization of the DBD

For the treatment, two discharge modes are used, which are referred to as the homogeneous DBD (HDBD) and filamentary DBD (FDBD). Fig. 2 gives images of the typical discharge modes. In the case of the HDBD, two glass planes of 3 mm in thickness covered both electrodes respectively and the air gap spacing was 2 mm, no filament was observed and the discharge was homogeneous in the whole discharge regime. In contrast, in the case of the FDBD, both electrodes were covered by two glass layers of 2 mm in thickness and the air gap spacing was 6 mm. It can be found that discharge phenomenon in Fig. 2a is different from that in Fig. 2b, where the filaments perpendicular to the electrodes are randomly distributed in the air gap. It should be pointed out that the photographs are taken by a commercial digital camera and not recorded by a high-speed CCD camera. In this paper, the photographs taken by a commercial digital camera are used to distinguish the two discharge modes [34,36].

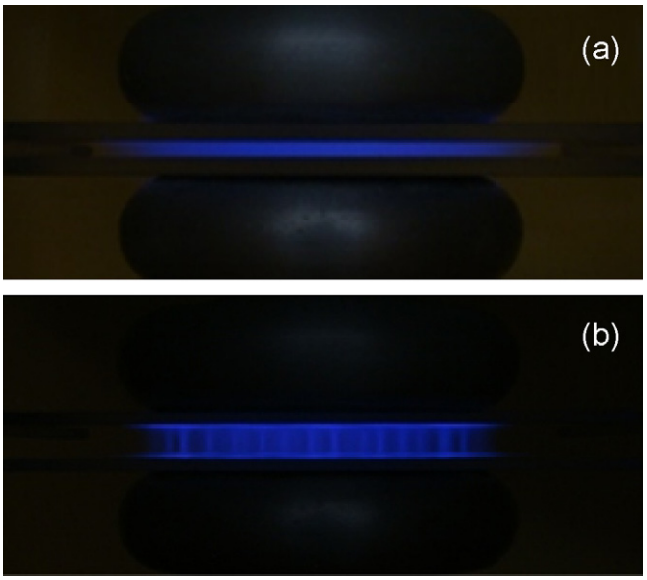

Fig. 2. Two typical DBD images during the treatment experiments: (a) the HDBD mode and (b) the FDBD mode.