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Atmospheric air plasma treated PBO fibers: Wettability, adhesion and aging behaviors

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ABSTRACT

Poly (p−phenylene-2, 6-benzobisoxazole) (or PBO) fibers were modified by air dielectric barrier discharge plasma (air-DBD) with different treatment time. The wettability of the PBO fibers were enhanced evidently, which was proved by dynamic contact angle analysis (DCAA), the contact angle in water of the fibers treated by air-DBD plasma decreased from 77.52° to 34.05°, while the surface free energy increased from 44.73 mJ/m^2 to 64.04 mJ/m^2. The surface morphology changes and variations of chemical components of PBO fibers were detected by scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). The results demonstrated that the fiber surface morphology became rougher and some newly polar groups were introduced onto the fiber surfaces. They contributed to the enhancement of the wettability. Furthermore, the interfacial adhesion between PBO fibers and bismaleimide (BMI) resin was improved obviously, which revealed by the increased ILSS of the PBO/BMI composites. Nevertheless, the ILSS of PBO/BMI composites decreased to 47.0 MPa after PBO fibers were stored in air for 7 days and there were little changes for 7−30 days.

1. Introduction

Plasmas have become increasingly popular in polymer surface modification recent years [1–3]. They have some advantages over other methods as follows: (1) environmentally friendly because of dry and clean processes; (2) relatively short treatment time; (3) low cost of energy and chemicals; (4) most importantly, they could generate desired effects without affecting the bulk properties of polymers [2–5]. However, low pressure plasmas have difficulties in realizing industrialization due to the high-expensed vacuum equipment and discontinuous operation mode. Nevertheless, atmospheric pressure plasmas can meet continuous production and operate without vacuum system in air [6], which provided possibilities for industrialization. As a consequence, some kinds of atmospheric pressure plasmas have been employed to modify polymer materials [7,8]. Among these plasmas, the dielectric barrier discharge (DBD) plasma was a promising one and attracted a lot of researchers [9–11].

PBO fiber was one kind of the advanced high-performance fibers, which has many advantages such as high modulus, high strength, excellent thermal and oxidative stability, etc., moreover, a long-term retain of these properties at high temperature was much attractive [12–14]. After developed by the US Air Force (USAF) in 1980s, PBO fiber has been considered as one of the most desired reinforcing materials in fiber-reinforced composites. However, the properties of the fiber/matrix composites were also impacted by interfacial adhesion between fibers and matrices and it influenced the transfer of loads from matrices to fibers [15,16]. Unfortunately, some characters of the PBO fibers such as smooth surface and chemically inactive component may do harm to the adhesion when preparing for fiber/matrix composites, as a result, many efforts have been applied to modify PBO fibers for decades, in order to enhance their wettability [16–18]. In this paper, PBO fibers were modified by a kind of atmospheric pressure plasmas, air dielectric barrier discharge (air-DBD) plasma, expecting to improve the hydrophilic properties of the PBO fibers and extend its practical applications. Nevertheless, the hydrophilic properties achieved by plasma treatment may vanish in a period of time after plasma treatment, which were called aging behaviors [19,20]. Therefore, it is necessary to investigate the aging behaviors of the plasma-treated PBO fibers.

PBO fibers were treated by air-DBD plasma with different treatment time. The wettability of the fibers were investigated by

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dynamic contact angle analysis (DCAA), corresponding changes of chemical components and morphology on PBO fibers were characterized by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM), atomic force microscopy (AFM), respectively. Adhesion between the PBO fibers and a promising thermosetting resin, bismaleimide (BMI) resin was studied by measuring interlaminar shear strength (ILSS) of the PBO/BMI composites. Furthermore, the changes of the PBO fibers after stored in air for 1–30 days were characterized by the ILSS values of the corresponding PBO/BMI composites.

2. Experimental

2.1. Materials

PBO fibers were received as HM (high modulus) yarn from Toyobo Co. Ltd., Japan. They were washed with acetone at room temperature for 48 h and then dried in an oven at 110 °C for 3 h before plasma processing.

BMI resin, a promising thermosetting resin, was supplied by AVIC Beijing Aeronautical Manufacturing Technology Research Institute, which was prepared by modifying 4,4′-diphenylmethane bismaleimide with polyether sulfone. The BMI resin was dissolved into acetone and 40 wt% for the resin in the BMI/acetone solution.

2.2. DBD plasma treatment

Fig. 1 shows the DBD plasma equipment used in our experiments. The plasma apparatus was comprised of a stainless hollow cylinder, two circular electrodes, a transmission system and a plasma generator. The plasma was produced by a plasma generator with an output frequency of 27 kHz. A hole on the cylinder ensured the system exposed to the atmosphere during the experiments. The electrodes were covered by two quartzes, which were used as the barriers, and the distance between them was 3 mm. Other essential parameters about the DBD apparatus are as follows: the electrode diameter was 4.7 cm so the volume of discharge area was 5.2 cm^3; the barrier thickness was 1 mm; the discharge power density [21] was set at 30 W/cm^3 (the peak voltage was 14.6 kV); the treatment time was 6 s–24 s by the transmission system (in order to decrease the treatment time, the fiber was designed to go through the discharge region four times and every treatment time was 1.5 s–6 s). Therefore, the short treatment time was beneficial for its application in industrialization.

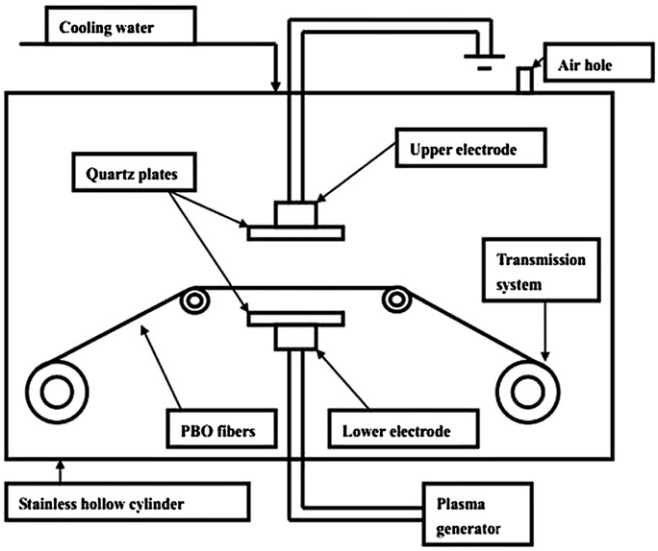

Fig. 1. DBD plasma apparatus.

2.3. Characterizations

2.3.1. Dynamic contact angle analysis

The dynamic contact angles and corresponding surface free energy of PBO fibers were studied by a dynamic contact angle analysis system (DCA-322, Thermo Scientific). Two liquids, water and diiodomethane, were used as polar and nonpolar solvents in the tests, respectively. Their surface tensions are 72.3 mN/m^2 and 50.8 mN/m^2.

The surface free energy of all samples was calculated from the following Eqs. (1) and (2) [22]:

$$\gamma_l(1+\cos\theta) = 2\sqrt{\gamma_s^p\gamma_l^p} + 2\sqrt{\gamma_s^d\gamma_l^d} \quad (1)$$

$$\gamma_{total} = \gamma_s^p + \gamma_s^d \quad (2)$$

where θ represents the dynamic contact angle between fiber and the testing liquids, γ_l is the surface tension of testing liquids, γ_{total} is the total surface free energy of fibers while γ_s^p and γ_s^d are its polar and dispersive components, respectively.

2.3.2. Chemical component analysis

X-ray photoelectron spectroscopy (XPS; ESCALAB 250, Thermo) was used to study the surface chemical compositions of PBO fibers. The XPS spectra were acquired by using an Al Kα ($h\nu = 1486.6$ eV) X-ray monochromatic source, and the accelerating voltage was 15 kV. The running vacuum was below 3.0×10^{-9} mbar. Spectra were obtained at a take-off angle of 90° relative to the fiber surfaces. The pass energy and step energy were 20 eV and 0.1 eV, respectively.

2.3.3. Morphology of PBO fibers

Scanning electron microscopy (SEM; QUANTA 200, FEI) and atomic force microscopy (AFM; Picoplus II, Agilent) were chosen to observe the PBO fiber morphology. The magnification of SEM was set at 5000×. The microscope was operated under 60 Pa with accelerating voltage of 20 kV. The AFM was in tapping mode. The arithmetic and root mean roughness (R_a and R_q) were calculated by the instrument software.

2.3.4. Adhesion of PBO fiber and BMI resin

2.3.4.1. Composites preparation. The PBO/BMI composites were prepared as follows: (1) PBO fibers were impregnated through BMI/acetone (40 wt%) solution. (2) The unidirectional prepregs were dried in a vacuum oven at 40 °C for 1 h to remove the solvents. (3) The composites were prepared by compression molding at 130 °C for 1 h, 190 °C for 3 h, and 230 °C for 3 h.

2.3.4.2. ILSS of composites. The interlaminar shear strength (ILSS) of PBO/BMI composites was measured by the three-point, short-beam bending test method to estimate the adhesive strength of the composites, according to ASTM D 2344. Specimen dimensions were 25 mm × 6 mm × 2 mm, with a span to thickness ratio of 5. The specimens were tested at a constant cross-head movement rate of 2 mm/min. ILSS values were calculated as follows:

$$\tau = \frac{3P_b}{4b\cdot h} \quad (3)$$

where τ is the interlaminar shear strength, P_b is the maximum compressive load, b and h are the width and thickness of the