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Surface treatment of aramid fiber by air dielectric barrier discharge plasma at atmospheric pressure

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ABSTRACT

Aramid fiber samples are treated by air dielectric barrier discharge (DBD) plasma at atmospheric pressure; the plasma treatment time is investigated as the major parameter. The effects of this treatment on the fiber surface physical and chemical properties are studied by using surface characterization techniques. Scanning electron microscopy (SEM) is performed to determine the surface morphology changes, X-ray photoelectron spectroscopy (XPS) is analyzed to reveal the surface chemical composition variations and dynamic contact angle analysis (DCAA) is used to examine the changes of the fiber surface wettability. In addition, the wetting behavior of a kind of thermoplastic resin, poly(phthalazinone ether sulfone ketone) (PPESK), on aramid fiber surface is also observed by SEM photos. The study shows that there seems to be an optimum treatment condition for surface modification of aramid fiber by the air DBD plasma. In this paper, after the 12 s, 27.6 W/cm^3 plasma treatment the aramid fiber surface roughness is significantly improved, some new oxygen-containing groups such as C–O, C═O and O═C–O are generated on the fiber surface and the fiber surface wettability is greatly enhanced, which results in the better wetting behavior of PPESK resin on the plasma-treated aramid fiber.

1. Introduction

Aramid fiber, combining high specific modulus and strength with excellent thermal stability and chemical inertness, is one of the best candidates as reinforcement for high-performance composites. However, the employing aramid fiber as reinforcement has been limited by poor fiber/matrix interfacial adhesion, because of the fiber having smooth surface and inert chemical structure, which prevents interfacial bonding with most of the commercially available resins used in composites [1–5]. In order to optimize the aramid-fiber/matrix adhesion, a variety of research efforts have been directed towards the improvement of fiber surface properties by various surface treatment techniques [6–11]. Traditional chemical treatments are often accompanied by the use of water and/or organic solvents, thus pose such problems as the disposal of drained water and recovery of organic solvents, which are energy-, time- and cost-intensive and involve pollution of water resources. Therefore, non-thermal plasma technology, which is efficient and environmentally friendly, has been extensively studied [12,13].

Plasma techniques may work in very flexible conditions. In comparison with that at low and medium pressure, plasmas at atmospheric pressure are predominantly studied recently, e.g. dielectric barrier discharge (DBD) plasma, which can not only separate the fiber bundles into individual filaments and modify the fiber surface without altering the bulk properties, but also has the advantages of operating at atmospheric pressure and easy formation of uniform and stable plasmas, avoiding the need of expensive vacuum equipment and permitting continuous processing of fiber surfaces. This approach has proved to be a promising method and is increasingly used for polymeric fiber or film surface modifications [14–16]. However, until now, only little research [17,18] is done on the relationship between the air DBD plasma treatment and the surface properties of aramid fiber.

In this paper, the influence of DBD plasma treatment in air at atmospheric pressure on aramid fiber surface is studied. Various different treatment durations have been explored to optimize the modification, and the physical and chemical changes on the treated fiber surface induced by the plasma are investigated. The surface morphology was examined using scanning electron microscopy (SEM), the surface chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS), and the surface wet-

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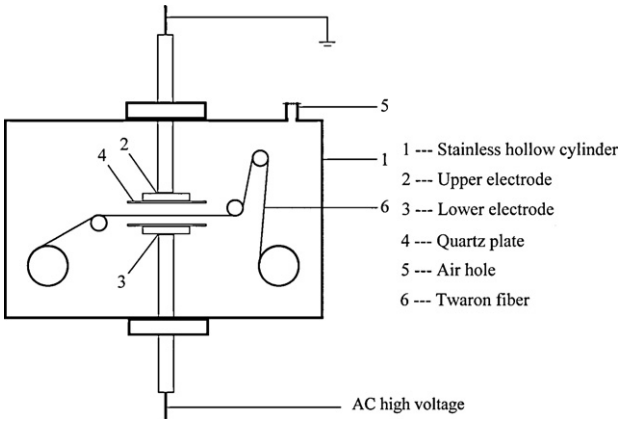

Fig. 1. Schematic representation of the air DBD plasma set-up.

tability was measured by dynamic contact angle analysis (DCAA). In addition, the wetting behavior of a kind of thermoplastic resin, poly(phthalazinone ether sulfone ketone) (PPESK), on aramid fiber surface was also illustrated by SEM photos.

2. Experimental

2.1. Materials

Twaron aramid yarn used in this study was received from Akzo Nobel Co. Ltd., Arnhem. The fiber samples were cleaned with acetone at room temperature before proceeding air DBD plasma surface modification in order to remove the surface oily finish, and then they were dried in an air oven at 110 °C for 3 h. The resin of which the wetting behavior on Twaron fiber was observed was thermoplastic poly(phthalazinone ether sulfone ketone), which was supplied by Dalian Polymer New Material Co. Ltd., China.

2.2. Air DBD plasma treatment

The schematic diagram of the dielectric barrier discharge apparatus is shown in Fig. 1 and the detailed description about the set-up was reported in previous work [18]. When a high AC voltage with an output frequency of 27 kHz was applied continuously, a filamentary dielectric barrier discharge would take place, which was uniform and stable. Twaron fiber samples were treated by means of going through the DBD plasma region at a constant speed. During the treatment process the system was always exposed to atmosphere through the air hole of the DBD experiment set-up.

The essential parameters about the DBD apparatus are shown in Table 1. The treatment durations were successively set as 6 s, 12 s and 18 s, which was carried out by the fiber entrainment speed being 1.56 cm/s and the fiber going through the discharge region two, four, and six times respectively with every treatment time lasting for 3 s. And it is important to note that after the air DBD plasma treatment the fiber samples kept staying in the DBD set-up for 12 h in order to incorporate more oxygen from the environmental atmosphere according to the post-plasma oxidation effect [19].

Table 1
Essential parameters about the DBD treatment in this study.

Parameters	Description
Electrode diameter (material)	4.7 cm (steel)
Discharge gap	0.3 cm
Barrier thickness (material)	0.1 cm (quartz)
Discharge power (power density)	143.5 W (27.6 W/cm^3)
Discharge atmosphere and pressure	Air and at atmosphere pressure
Treatment time	0 s (untreated), 6 s, 12 s, 18 s

2.3. SEM

Scanning electron microscopy (SEM; QUANTA 200, FEI) was selected to observe the surface morphologies of Twaron fiber. And the wetting behavior of the PPESK resin on the fiber filaments was also studied by SEM photos; the samples were prepared by impregnating the filaments with PPESK solution which was made by dissolving the PPESK resin into *N,N*-dimethylacetamide (DMAc) solvent, and then drying the fiber/resin samples in an air oven (120 °C/1 h, 175 °C/3 h) to remove DMAc completely; it is important to note that the volume fraction of Twaron fiber in every sample was set to about 60%. The pressure of the chamber for SEM measurement was less than 60 Pa and the magnification was set at 5000×.

2.4. XPS

The surface chemical composition of Twaron fiber was analyzed by X-ray photoelectron spectroscopy (XPS; ESCALAB 250, Thermo), making use of monochromatic Al Kα ($h\nu$ = 1486.6 eV) X-ray source (15 kV, 250 W) radiation from a dual Al–Mg anode. The measurements were performed at an operating vacuum lower than 3.0×10^{-9} mbar. Spectra were acquired at a take-off angle of 90° relatively to the sample surface. The pass energy and energy step set for elemental quantification were 100 eV and 1 eV, respectively, and for C1s peak shape identification purpose the pass energy and energy step were fixed at 20 eV and 0.05 eV, respectively. The non-linear least squares fitting (NLLSF) program with a Gaussian–Lorentzian production function was used for curve fitting of C1s spectra.

2.5. DCAA

The surface free energy and contact angles of Twaron fiber were measured through a dynamic contact angle analysis system (DCAA; DCA-322, Thermo). The fiber sample was cut into about 1 cm in length and fixed indirectly to a wire hook suspended from the microbalance of the system. The fiber was immersed into the testing liquid media by raising the elevating stage at a constant speed of 1 mm/min and then the dynamic contact angles (θ) were obtained schematically by the measurement. There are two equations (Eqs. (1) and (2)) as follows, from which the surface free energy can be calculated:

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

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

where θ is the dynamic contact angle between fiber and testing liquid which is calculated by the computer program, γ_l is the surface tension of the testing liquid, γ_{total} stands for total surface free energy of the fiber, and γ_s^p and γ_s^d are the polar component and the dispersive component of total surface free energy, respectively [20]. In our experiment, water (polar solvent; its surface tension is 72.3 mN/m) and diiodomethane (non-polar solvent; its surface tension is 50.8 mN/m) were chosen as testing liquids.

3. Results and discussion

3.1. Surface morphology of Twaron fiber

SEM was used to investigate the surface morphology changes of Twaron fiber before and after the air DBD plasma treatment. In Fig. 2 is shown a comparison of the SEM images of the untreated fiber and