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Optimization and characterization of poly(phthalazinone ether ketone) (PPEK) heat-resistant porous fiberous mat by electrospinning

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A B S T R A C T

Poly(phthalazinone ether ketone) (PPEK) is noted for its outstanding heat-resistance property and mechanical strength. A one-step electrospinning method was conducted to produce PPEK micro-nano porous fibrous mat. We gave emphasis study on the spinnability, optimized conditions, fibers' morphology, surface science and fracture mechanism. The uniform electrospun fibrous mat resulted from PPEK/chloroform binary system indicated that PPEK would be a prospective material to be applied in electrospinning. Addition of a small amount of non-solvent (ethanol) turned out to be advantageous to the reduction of fiber diameter and the alleviation of choking during spinning process. Organic salt (benzyltrimethylammonium chloride) was employed to increase the conductivity of solution for the formation of thin fiber. After trials, PPEK/chloroform/ethanol system with salt and PPEK/NMP system were taken as two optimized systems. These two systems showed different pore fraction in N_2 adsorption test, and displayed different mechanical behaviors in uniaxial tension test. The fibrous mat from PPEK/chloroform/ethanol system showed a feature of ductile fracture with relatively low fracture strength but long fracture deformation, while the fibrous mat from PPEK/NMP system showed a feature of brittle fracture with small deformation but quite large fracture strength of ca. 6 MPa. Finally thermogravimetric analysis indicated that the resultant PPEK fibrous mat did not decompose until the temperature reached 478 °C, which qualified the resultant fibrous mat as a promising material used under high-temperature condition.

1. Introduction

Electrospinning has been proved to be an efficient and controllable method to produce polymer and composite nanofibrous mats with large specific surface area and high surface roughness. The electric field employed in this technique enables the fiber formation from a solution jet when the electrostatic force of the solution jet overcomes the surface tension and viscoelastic force [1].

The morphology of the electrospun fiber has strong dependence on the solution properties (e.g. viscosity, electrical conductivity and so on) and the electrospining parameters (e.g. voltage, flow rate, humidity and so on). For example, Niculae and Liliana [2] found that micro-/nanoparticles and uniform fibers were produced by electrospinning of cellulose acetate phthalate when 2-methoxythanol and acetone-water mixture were used as solvent respectively. A void hemispheres-like structure changed into beaded fiber and beadless fiber with the increase of the solution concentration. The electrospinnability of cellulose acetate phthalate from the 2-methoxyethanol was better than that from the acetone-water mixture. Lu et al. [3] performed a simulation of the electrospinning of ethylene/vinyl alcohol copolymer to investigate the effect of solvent. Their results showed a certain configuration transform barrier should be overcome, which was determined by the various relaxation time of the polymer chain in solvent during the electrospinning process. A shorter relaxation time resulted in a more fierce solution jet whipping and thinner fibers. Besides, phase diagram [4] and Hansen solubility parameters [5] were also taken as effective approaches to study the effect of solvent on electrospinning.

Furthermore, the morphology of the electrospun fibers was also influenced by additive [6,7]. Gupta et al. [7] revealed that nylon-6/nitromethane solution could be electrospun in the presence of gallium trichloride and porous fibers were obtained after the gallium trichloride was removed. This kind of Lewis acid not only facilitated the formation of the porous structure, but also prevented the nylon-6 molecules from crystallization via intermolecular hydrogen bonds, which promoted fiber formation.

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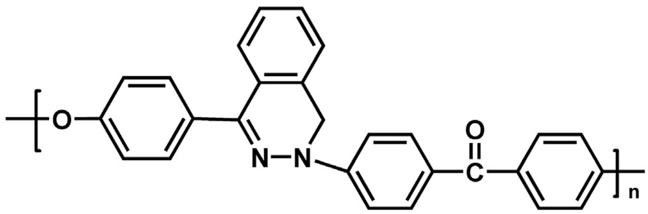

Fig. 1. Chemical structure of PPEK that we used as raw material.

Numerous kinds of synthetic polymers have been employed in electrospinning, including polystyrene (PS) [8], polyvinyl alcohol (PVA) [9], polyester (PET) [10], polyacrylonitrile (PAN) [11], and so on. At the same time, a variety of natural macromolecules have been performed in the preparation of nanofibers by electrospinning, such as cellulose [12] and silk fibroin [13]. Moreover, various inorganic nano particles, such as titanium dioxide [8] and silica [14] were selected in electrospinning to prepare functional composite nanofibers.

PPEK containing phthalazinone moieties (see Fig. 1) is a kind of novel soluble polymer with the highest heat-resistance level in the world at present to our knowledge [15,16]. The twisty and non-coplanar structure of the PPEK monomeric unit enables it soluble in chloroform, *N*-methyl-pyrrolidone (NMP) and some other organic solvents, which expands its processing method greatly [3,15–17]. Therefore, PPEK has been regarded as a candidate of great potential for heat-resistance and corrosion-resistance applications in many areas, such as aerospace and power battery.

Currently, dense and asymmetric PPEK films produced by phase inversion and hollow fibers prepared by spinning showed excellent gas and liquid separation ability as permeation and filtration unit [18] as well as ion exchange membrane with good cell performance [19]. However, electrospun nanofibrous mats of PPEK that exhibiting outstanding heat-resistant property has not been considered yet.

Herein, a novel kind of micro-nano fibrous mat prepared from PPEK with inherently excellent heat-resistant property by electrospinning method was reported in this study. For the first time, the optimum electrospinning solution systems were determined by trials for different solution recipes with the addition of non-solvent and organosoluble salts, followed by the contrastive investigation into their surface characteristics and mechanical properties.

2. Experimental

2.1. Materials and solution preparation

PPEK powder with molecular weight of 4.63×10^4 (*M*n) was provided by Dalian Polymer New Material Co., LTD. The molecular weight of PPEK powder was measured at 40 °C with chloroform used as eluent (1 mL/min) and polystyrene used as standard on a gel filtration chromatography (GPC) (Agilent PL-GPC50). Chloroform, ethanol, benzyltrimethylammonium chloride (BTMAC) and *N*-methyl-2-pirrodone (NMP) were purchased and used as received without further purification. All solutions were prepared using an Erlenmeyer flask in ambient condition.

The PPEK/chloroform solution of various concentration were prepared by dissolving PPEK in 10 mL of chloroform followed by vigorous stirring at room temperature to form homogenerous solutions. The same procedure was performed for the polymer/solvent/non-solvent ternary system, where ethanol was added as a non-solvent in a volume ratio of 1.5:9 (ethanol:chloroform). In addition, BTMAC was also added to the ternary system with a varying weight fraction from 1 wt% to 5 wt%. The PPEK/NMP solution was prepared at 140 °C in the same way as the preparation of PPEK/chloroform solution.

2.2. Characterization of the electrospinning solutions

The electrical conductivity of the electrospinning solutions was measured with two machines combined with different ranges: R6441A Digital multimeter and HP 4339B High Resistivity Meter for resistance lower and higher than 10^7 Ω, respectively. All measurements were performed in ambient condition. All the solutions were stirred for 4 h with a Teflon-coated magnet to ensure that dissolution equilibrium was reached prior to the electrical conductivity measurement.

The viscosity of the homogeneous solutions for electrospinning was measured with a rotary viscosimeter (NDJ-1, Shanghai Jingke) after the deformation of solutions.

2.3. Electrospinning

The electrospinning of the PPEK solutions was carried out on a single-spinneret electrospinning setup. Solutions were loaded into a 10 mL syringe with a blunt-ended stainless steel needle, which was mounted on a pump (LSP01-1C, Longer Pump Ltd.). The high-voltage supplied by a power (TE4020, Teslaman HVPS Co., Ltd.) was applied between the needle tip and the grounded aluminum foil collector, and the power supply was connected to the syringe needle via an alligator clip. All experiments were carried out on a horizontal electrospinning set-up at room temperature, and the processing parameters for different electrospinning solutions are listed in Table 1.

2.4. Characterizations of electrospun fibers

The morphologies of the samples were investigated with a scanning electron microscope (SEM) (SEM 450, FEI company, USA) at an accelerating voltage of 20 kV. The as-spun fibers were stuck directly onto the SEM holder by conductive adhesive followed by gold coating. Thirty points were taken for every sample to determine the average fiber diameter with a Nano Measurer software.

Specific surface area was evaluated by the Brunauer-Emmett-Teller (BET) equation. The samples were pretreated at 393 K for 2 h under N_2 purgation. Then, adsorption measurement was operated with a high precision adsorption measuring apparatus (BELSORP-mini, BEL Japan, Inc.).

Uniaxial tension test was conducted under atmospheric conditions using a single fiber strength tester (Laizhou electric instrument Co., Ltd.) with rectangular shaped samples of 30 mm in length and ca. 7 mm in width.

Thermogravimetric analysis (TGA) was conducted with a thermogravimetric analyzer (TA Q500, American) under N_2 atmosphere from room temperature to 800 °C at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Solution characterization

Enough polymer chain entanglement is required for the production of smooth electrospun fiber, which was ascribed to the effect of solution concentration [1,4]. Therefore, a primary solution concentration optimization was conducted for different solvent system after a series of trials. Afterwards, polymer solutions containing 8 and 9.5 wt% PPEK for PPEK/chloroform binary system, 5, 7, 8, 10 wt% PPEK for PPEK/chloroform/ethanol ternary system, and 20 wt% PPEK for PPEK/NMP binary system were prepared as representative samples. All these solutions were dissolved completely without phase separation.