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Low-surface-free-energy polybenzoxazine/polyacrylonitrile fibers for biononfouling membrane

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ABSTRACT

We blended poly(3-phenyl-3,4-dihydro-2H-1,3-benzoxazine) (PBA) into polyacrylonitrile (PAN) to generate low-surface-free-energy fibers without fluorine and silicon elements for electrospinning. Liquid-state BA at room temperature can be solidified in electrospinning process using PAN as a medium through their miscible behavior. Results indicate that the mixing below 50 wt% BA into PAN matrix for electrospinning has no significant dropping beads, indicated a miscible PAN/BA system. Above 70 wt% BA in PAN solution could not be solidified completely after electrospinning, revealed apparent beaded fibers. The PAN/PBA blend fibers, obtained after curing at 300 °C, generated a superhydrophobicity because of the low-surface-free-energy PBA. In addition, laser scanning confocal microscope (LSCM) measurements were included to determine the relative amount of antibody that adsorbed to these PAN/PBA fibers to examine the biofouling-resistant property. The results showed an obviously decreased protein adsorption with increasing PBA fraction. The correlations between PAN and PBA would provide insight into the designing and developing of low-surface-free-energy fibers without fluorine and silicon elements to improve biofouling-resistant property.

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1. Introduction

Superhydrophobic surfaces, which are characterized by static water contact angles higher than 150°, are divided into two classes. One is the "self-cleaning surface", which has a low sliding angle (i.e., small contact angle hysteresis). The self-cleaning surfaces have recently attracted much attention for their promising applications in various fields from daily life to industry [1]. The other superhydrophobic surface is the one with "high adhesion to water". Highly adhesive surfaces show both high water contact angle and large contact angle hysteresis. In contrast to the self-cleaning surfaces, the studies of such superhydrophobic surfaces are very limited [2]. As representative examples, a superhydrophobic polystyrene nanotube layer was aligned via template-wetting method [3], and superhydrophobic poly(propylene) surfaces with tunable sliding angles were fabricated by controlling shear and thermal conditions [4].

The fabrication or functionalization of superhydrophobic surfaces are of significant interest because of the potential utility of these nonwetting materials in a broad range of consumer, industrial, and medically oriented contexts (e.g., the design of "self-cleaning" surfaces and textiles, new nonfouling surfaces, and membranes for oil/water separation, etc.). Several methods have been used to fabricate superhydrophobic surfaces, including sol–gel processing [5], chemical vapor deposition [6], lithography [7], chemical etching [8], self-assembly [9], and electrospinning [10]. Except for the last, all of these methods are complicated and require special equipment, high temperature or vacuum conditions, or low-surface-free energy material modification involving multiple steps, which makes it difficult for practical applications in large-scale coatings. Electrospinning offers a versatile approach to fabricate unique micro and nanostructures with interesting wetting characteristics. The nanofibrous mats can be used for a broad range of applications such as filtration [11], composite materials [12], tissue engineering [13], sensor systems [14], etc.

Several approaches have been reported for combining materials of low surface energy with high surface roughness, such as electrospinning hydrophobic (PFDA-co-AA) random copolymer and polyacrylonitrile (PAN) as the second one [15] and poly[bis(2,2,2-trifluoroethoxy) phosphazene] [16] into fibrous substrates with suitable morphologies so as to make the surface superhydrophobic with or without subsequent chemical treatment. These above processes prepared superhydrophobic fibers by electrospinning certain hydrophobic polymers [17], or coating with potentially

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hazardous fluoro groups [18]. Polybenzoxazine (PBA) is a recently discovered class of nonfluorine, nonsilicon, low-surface-free-energy polymeric materials [19]. Benzoxazine monomer, 2,2-bis(3-methyl-3,4-dihydro-2H-1,3-benzoxazinyl)propane, can be used to produce polybenzoxazine films by spin-coating and curing in an oven. The surface free energy of polybenzoxazine film is 16.4 mJ/m^2, which is even lower than that of PTFE by 21 mJ/m^2 [20,21]. Polybenzoxazine rarely dissolves in the solvent to manufacture as fibrous structure because of its cross-linking chains. In general, the BA can be used as a precursor to obtain polybenzoxazine films after curing. However, when BA liquid (solution) is drawn out of the tip of a nozzle, it cannot transform into a minuscule fiber upon drying or solidifying and form a nonwoven fabric on a collective target. Therefore, the practical applications of polybenzoxazine for electrospun super-hydrophobic mats are significantly limited. For improving the polybenzoxazine practical application of fibrous mats, PAN is an ideal blend material due to its high melting temperature [22]. In this study, we demonstrate a facile fabrication of a nonfluorine, nonsilicon fabric from electrospun fibers comprising of PAN and PBA, which is one of low surface energy polymers. Precursor fibers of PAN/BA hybrids with various BA fractions are generated by electrospinning. After curing PAN/BA hybrid fibers, PAN/PBA blend fibers can be obtained. To the best of our knowledge, this paper is the first report of an electrospun mat exhibiting a low surface energy without fluorine and silicon elements. These fibrous structures can be applied in diverse applications, including self-cleaning glasses and clothes, protection against corrosion of metallic parts, antiprotein adsorption and antisnow sticking.

2. Experimental section

2.1. Materials

Polyacrylonitrile (PAN) (Aldrich Co) with an average molecular weight (Mw) of 150.000 g/mol was used as received. Paraformaldehyde (Aldrich, 95%), phenol (Aldrich, 99.5%), aniline (Aldrich, 99.5%), and dimethylformamide (DMF) were used without further purification. Aniline (Acros, 99.5%) was distilled before use. N,N-Dimethylformamide (DMF) (Aldrich, 99.8%) were utilized as received. 3-phenyl-3,4-dihydro-2H-1,3-benzoxazine (BA) was synthesized and purified according to the procedure described elsewhere [23]. The synthesized BA was purified by dissolving in the 1 L diethyl ether, and washing three times with 1.5 L of aqueous 3 N sodium hydroxide, and finally five times with 1 L distilled water. The ether solution was dried with anhydrous sodium sulfate followed by evaporation of ether under vacuum to afford pale yellow liquid.

2.2. Preparation of electrospun PAN/PBA fibrous mats

The DMF solution with 10 wt% PAN was stirred for 1 h before use. Binary mixture experiments between BA and PAN were performed in DMF at increasing BA to PAN weight ratios: 0, 30, 50, 70 and 100 wt%. Dispersions of BA were added dropwise into PAN solution, and were stirred for 1 h at room temperature. The solution was filtered through a 0.2 μm syringe before both of electrospinning and spin-coating. The PAN:BA weight ratios for the various hybrids were 100:0, 70:30, 50:50, 30:70 and 100:0 in DMF solutions, denoted as P10B0, P7B3, P50B50, P3B7 and P0B10, respectively. The concentration of the PAN/BA hybrids in DMF solution was controlled at 10 wt% for P10B0, P7B3, P50B50, P3B7 and P0B10. For electrospinning, a syringe pump (KDS-100, KD Scientific. Co., Ltd.) was fixed to a support which could be moved rightward and leftward with a speed of 7 m/min along a slipway to jet the PAN/BA hybrid solution uniformly on a rolled cylinder substrate as films. The metal needle tips of the syringes were connected to the positive electrode of a high voltage power supply (YSTC Technology Co.). The feeding rate of polymer solutions was 1 mL/h. The applied voltage was 20 kV, and the tip-to-collector distance was 15 cm. The fibrous mats were collected on the surface of aluminum foil and dried at room temperature in vacuum for 24 h prior to the subsequent characterizations. The PAN/BA hybrid fibers involving P10B0, P7B3, P5B5, P3B7 and P0B10 were cured at 300 °C for 2 h under nitrogen environment to obtain poly(3-phenyl-3,4-dihydro-2H-1,3-benzoxazine) (PBA) blending with PAN as fibrous mats, denoted as P10PB0, P7PB3, P5PB5, P3PBA7 and P0PB10, respectively. In addition, the PAN/BA hybrid solutions were spin-coated onto a glass by immediate spinning at 1500 rpm for 30 s; they were then cured at 300 °C for 2 h under vacuum to obtain the PAN/PBA coating for comparison.

2.3. Miscibility and curing behavior of the PAN/BA hybrids

The PAN/BA hybrids were analyzed by Fourier transform infrared spectroscopy (FTIR) to assess their effects on thermal property. All spectra collected using FTIR of the PAN/BA hybrids were recorded using the KBr disk method. The FTIR spectra were recorded with a 8 cm^{-1} spectral resolution and degassed with nitrogen on a Digilab FTS-1000. A total of 20 scans were accumulated for signal-averaging of each IR spectral measurement to ensure a high signal-to-noise ratio. Peaks at δOH free, δOH intra HB, δOH inter HB, νNH inter HB, νNH intra HB, νN$^+$H intra HB were adopted to evaluate the interactions of PAN/BA and PAN/PBA systems by the de-convolution procedure (fitting function). The samples were further cured at 300 °C for 2 h to identify the formation of PAN/PBA blending by FTIR. Differential Scanning Calorimetry (DSC) analyses were performed on a Perkin Elmer (DSC 4000) in the range of 30–300 °C with heating rate of 10 °C/min under nitrogen flow to determine the curing temperature (Tc) of BA and degradation temperature (Td) of PAN, respectively. Approximately 5–10 mg sample was weighed and sealed in an aluminum pan. The sample was then quickly cooled to room temperature from the first scan and then scanned between 30 and 300 °C at a scan rate of 5 °C/min. Tc and Td were taken as the midpoint of the exothermal peaks.

2.4. Characterization and non-biofouling of the PAN/PBA fibrous mats

PAN/BA hybrid and PAN/PBA blend fibrous mats were observed through a field-emission scanning electron microscopy (FE-SEM) (JEOL, JSM 6500F) operating at 15 kV after platinum coating. The diameters of fibers were measured using image analysis software (Image-Pro plus). Static water contact angle (SWCA) measurements were performed by increasing the drop volume and recording the angle on a GH-100 Contact Angle System (KRÜSS GmbH LTD.). The SWCA was determined by fitting a Young–Laplace curve around the drop. The experiment was performed under normal laboratory ambient conditions, 35% relative humidity. The mean value was calculated from at least 10 individual measurements and the measurement error was less than 3°. In addition, it is well known that a heterogeneous surface (chemically or geometrically) usually shows contact angle hysteresis [24]. That is, for a geometrically rough surface, contact angle hysteresis originates primarily from the rough contact interface that depends upon the contact area of water with the structured surface. The earliest work to model liquid drops on a roughness surface can be contributed to Wenzel [25] and Cassie [26]. Their models are described by the following equations.

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