High filtration performance thin film nanofibrous composite membrane prepared by electrospraying technique and hot-pressing treatment

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ABSTRACT

For conventional powder coating technology, powder coating materials were directly coated onto the target surface and then heated and cured to form a coat. Inspired by this technology, a facile route for fabrication of thin film nanofibrous composite (TFNC) membrane consisting of a nanofibrous substrate and a hydrophilic barrier layer was developed by electrospraying poly(vinyl alcohol) (PVA) nanobeads onto the electrospun polyacrylonitrile (PAN) substrate and following by hot-pressing treatment assisted by moistening absorption. Water molecules from absorbed moisture acted as "plasticizer" and could facilitate PVA melting. The moistened electrosprayed PVA nanobeads could be easily melted or softened to be pressed imperceptibly into an integrated barrier film on the supporting layer at a certain temperature. The depositing time of PVA electrospraying, moistcuring time, thermal treatment temperature and time were optimized to achieve an integrated, nonporous PVA barrier layer. The resulting barrier layer was chemically crosslinked and its filtration performance can be finely controlled by different PVA crosslinking degree. Especially, the optimized PVA/PAN TFNC membrane possessed high ultrafiltration performance in BSA filtration tests with water flux 173.0 L/m²h and rejection above 98.0% at low feeding pressure 0.3 MPa. This work may provide a practical feasibility for water filtration application.

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1. Introduction

It is generally acknowledged that the shortage of clean, fresh water has led to many serious problems and attracted increasing worldwide attention [1,2]. Filtration technology has become one of the most important technologies for making fresh water and has achieved great progress in recent decades [3–5]. High rejection and high flux are the major targets in preparing filtration membranes. To increase the ultrafiltration/nanofiltration efficiency, the composite filtration membranes with a hierarchical structure have drawn much attention in water treatment [3,6] due to their priorities of high rejection, good permeability and pressure resistance.

The composite membrane usually consists of a porous low resistant substrate offering mechanical support and a thin top barrier layer offering filtration function [6–8]. Different materials and preparation methods can be chosen to prepare the substrate and the top layer separately, thus optimizing the entire membrane

performance. Conventionally, the porous substrate of the composite membrane is asymmetric porous membrane which was prepared by phase inversion techniques. Nanofibrous membranes obtained from electrospinning are promising candidates as porous substrate for composite membranes due to their unique properties of large porosity, high surface-to-volume ratio, interconnected pore structures, environmentally benign nature and so on [9–11], which may enable them to have high permeability and low energy cost in water filtration applications. Actually, it has been demonstrated that electrospun nanofibrous membranes are excellent candidates as the porous supporting layer for thin film composite membranes with high filtration performance [12–16]. For the fabrication of this kind nanofibrous thin film composite membrane, interfacial polymerization [12,13] or surface coating [14] is always performed to prepare hydrophilic barrier layer, especially, surface coating is a very common way for the anti-fouling barrier layer preparation. However, easy penetration of the coating solution into the highly porous nanofibrous substrate is hardly avoided which results in a much thicker barrier layer. Various methods, such as casting solution just before fast gelling time [15,16] and

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coagulant soaking method [17–19], were performed to minimize the penetration of the cast solution to achieve the coating barrier layer as thin as possible in typical surface-coating fabrication. In our previous report, a novel route (shown in Fig. S1) [20] was proposed to fabricate ultra-thin barrier layer on nanofibrous substrate by electrospraying hydrophilic polymer nanofibers or nanobeads combined with solution treatment [20,21]. The electrosprayed polymer nanofibers or nanobeads would absorb enough solvent and be swollen to merge imperceptibly into a thin film layer on the surface of nanofibrous substrate. The barrier layer film of the resultant membranes was relatively incompact due to its film formation process by polymer swollen so that it could be very suitable for ultrafiltrating the systems with particle size relative larger than 10 nm like oil/water emulsion (size: 10–50 nm, analyzed from SEM images in Fig. S2). For filtrating relatively small organic molecular (size: 1–10 nm) from water system, a relatively compact barrier layer for the TFNC membranes should be achieved by precisely regulating the filtration performance of the top barrier layer for desirable high flux with high organic rejection.

As we know, electrostatic powder coating is a very popular and mature technique which has been widely used in a great variety of industries such as those manufacturing automobile, garage doors, office furniture and so on in last decades [22–26]. Traditionally, the powder coating process involves the deposition of powdery coating materials onto a substrate surface and a curing phase at a high temperature to achieve a continuous intact film [26–28]. Sometimes, low temperature plasticizers or melting additives were introduced to promote the film formation. Inspired by this technique, a facile scale-up method was developed to fabricate the TFNC membrane by slightly pressing the melted or softened electrosprayed nanofibers or nanobeads to form an ultrathin integrated barrier on the nanofibrous supporting substrates through hot-pressing treatment. Obviously, it should be much easier to gain a more compact top layer film for composite by nanobeads hot-press film-formation process than by solution treatment (In solution treatment from literature [20], the integrated top layer film was formed by nanobeads being swollen and merged imperceptibly and naturally). Herein, hydrophilic PVA was still used to act as the coating material on PAN nanofibrous substrate for composite filtration membrane preparation by electrospraying technique combined with hot-pressing treatment. However, it is not easy to melt PVA directly because the melting point of PVA is very close to its decomposition temperature owing to the multi-hydroxyl structure of PVA [29–31]. In fact, some small molecular plasticizers were often used to improve the melt-processability of PVA [30–32]. Wang et al. [32] suggested that water can break the intermolecular hydrogen bonds of PVA and decrease the interactions of PVA, and has a plasticizing effect through molecule movement. Here, the electrosprayed PVA nanobeads top layer would be melted with the aid of the moisture (water molecules diffused into the PVA nanobeads acting as the plasticizer to facilitate the PVA melting) to fuse imperceptibly into an integrated barrier film on the supporting nanofibrous layer at a certain temperature below its melting point. The depositing time of PVA electrospray, the moistcuring time, heating temperature and curing time during the thermal treatment process were optimized to achieve the integrated and nonporous PVA barrier layer. The resulting PVA barrier layer was chemically crosslinked and the filtration performance of the resultant TFNC membrane was evaluated by water systems with organic molecular size below 10 nm such as bovine serum albumin (BSA) or Vitamin B_{12} water solution.

2. Experimental details

2.1. Materials

PAN ($M_w = 120{,}000$) was kindly supplied by Shanghai Jinshan Petroleum Chemical Co., Ltd., and was heated in vacuum drying oven for 24 h at 40 °C before use. PVA ($Mw = 146{,}000$–$186{,}000$, degree of hydrolysis=99%), vitamin B_{12}, Triton X-100 were obtained from Aldrich. N,N′-dimethylformamide (DMF), acetone, glutaraldehyde (GA, 25 wt% aqueous solution) and hydrochloric acid (HCl) were purchased from Shanghai Chemical Reagent Plant. Bovine serum albumin (BSA) with a molecular weight of ca. 67 kDa was bought from J&K Chemical. All chemicals mentioned above were used without further purification.

2.2. Fabrication of PVA/PAN TFNC membrane for filtration

Inspired by conventional powder coating technology, a new, simple and controllable fabrication process was proposed to prepare the composite membranes containing PVA barrier layer and PAN nanofibrous substrate. The schematic illustration of the fabrication process was shown in Fig. 1. Firstly, a hydrophilic PVA top layer was electrosprayed onto the surface of PAN nanofibrous substrate to form PVA/PAN double-layer mat and their detailed preparation process had been described in our previous reports [20,21]. The electrospun PAN nanofibrous mats acting for supporting layers were cut into sizes of 7 cm × 7 cm and then cold-pressed at room temperature at 6 MPa for 30 s to improve their mechanical strength and obtain smooth surface for the further preparation of PVA barrier layer. The thickness of the as-prepared PAN nanofibrous mats was about 40 μm. Secondly, the PVA top layer was moistened by absorbing moisture in a moistener with humidity of ~90% and then sandwich heated by two hot plates controlled at a certain temperature for some time to melt and to be pressed into an integrated layer under the weight pressure of hot plate (~0.02 MPa). Finally, the as-prepared PVA/PAN composites were crosslinked by different concentration GA in water/acetone (5/5 in volume) solution at the pH of 1.5 for 1 h. The resulting composite membranes were washed with pure water and kept in the water before use. The filtration performance of PVA barrier layer was finely controlled by the crosslinking degree of PVA and the resultant composite membrane exhibit different filtration performance. The highly crosslinked PVA (HCPVA, with GA concentration ranging from 1.0 wt‰ to 6.0 wt‰) TFNC membrane was used to separate vitamin B_{12} with molecular weight of 1355.4, while the lowly crosslinked PVA (LCPVA, with GA concentration ranging from 0.4 wt‰ to 1.2 wt‰) TFNC membrane was used for ultrafiltrating BSA solution.

2.3. Characterization

The porosity of the electrospun PAN nanfibrous membrane can be calculated with the Eq. (1):

$$Porosity(\%) = \frac{\rho_0 - \rho}{\rho_0} \times 100\% \tag{1}$$

where ρ is apparent density of PAN nanofibrous membrane, which can be calculated according to the weight and volume of the membrane with following equation:

$$\rho = \frac{m}{v} \tag{2}$$

where m and v are the weight and the volume of the nanofibrous membrane, respectively. ρ_0 is density of PAN. The sizes of dried membrane for evaluation are 7 cm × 7 cm (length × width) and at least 4 pieces of each membrane were tested.