



Low pressure high flux thin film nanofibrous composite membranes prepared by electrospraying technique combined with solution treatment

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ABSTRACT

In this study, high flux thin film nanofibrous composite (TFNC) membrane consisting of a nonwoven nanofibrous supporting layer and a thin hydrophilic barrier layer was developed and used as an ultrafiltration media to separate an oil/water emulsion at low feeding pressure. Firstly, the hydrophilic barrier layer was fabricated by electrospraying polyvinyl alcohol (PVA) on nanofibrous polyacrylonitrile (PAN) substrate. Secondly, the deposited PVA top layer was swollen to merge imperceptibly into an integrated barrier film on the supporting layer by immersing PVA/PAN double-layer membranes into suitable solvent water and nonsolvent acetone mixture, and then chemically crosslinked by glutaraldehyde in water/acetone solution. The water content of water/acetone solution and the immersion time were optimized to achieve the integrated and nonporous PVA barrier layer. Filtration performance of the resulting PVA/PAN TFNC membranes was evaluated by the oil/water emulsions separation system. Results showed that the optimized TFNC membrane possessed high flux (347.8 l/m² h) with high rejection rate (99.6%) at very low feeding pressure (0.2 MPa). It is believed that the strategy for fabricating TFNC membranes described here can be extended easily to fabricate TFNC membranes from many other polymeric membrane materials simply by choosing the suitable solution system for post-treatment.

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1. Introduction

Highly porous nonwoven nanofibrous membranes possess low basis weight, high permeability and small pore size that make them appropriate for a wide range of filtration applications [1]. It should not be a surprise that nonwoven nanofibrous scaffolds have attracted a great deal of attention in filtration application. Kaur et al. [2] compared the filtration performance of polyvinylidene fluoride (PVDF) electrospun nanofibrous membrane and commercial PVDF membrane with same mean pore size. Water filtration results revealed that the electrospun nanofibers membrane possessed a better flux throughput than the commercial PVDF microfiltration membrane with the same mean pore size. However, it is difficult for nanofibrous membranes to be used directly as ultrafiltration or nanofiltration membrane although they have high permeability and completely interconnected pores which make them appropriate for microfiltration applications [3–5]. The reason is that the pore size of most nanofiber membranes was difficult to be reduced to less than 100 nm, which can only remain the particle with size of more than 300 nm according to the correlations between membrane pore size and fiber diameter in a non-woven structure, i.e., the mean pore size was about 3 ± 1 times the mean fiber diameter,

and the maximum pore size was about 10 ± 2 times the mean fiber diameter [6].

For water filtration, the thin film composite membrane is one of the preferred formats for conventional UF or NF media consisting of an asymmetric porous membrane to provide filtration functions (often fabricated by the phase inversion method) and a barrier layer (fabricated by coating or interfacial polymerization) to provide selectivity [7,8]. As can be imagined, nanofibrous thin film composite membranes exhibit a much higher flux rate for water filtration than that in the conventional thin film composite, involving the use of nonwoven nanofibrous mat with higher surface porosity and water permeability [9,10] to replace the flux-limiting asymmetric porous membranes, assuming that the barrier layer thickness are similar for both kind of thin film composites. Actually, it has been demonstrated that highly liquid-permeable electrospun nanofibers membranes were excellent candidates as the porous supporting layer under the top barrier layer to provide high flux thin film composite membranes [11–13]. The key point for preparing such nanofibrous composite membranes was to achieve a desirable minimum thickness of barrier layer. However, the preparation of an appropriate thin barrier layer on the highly porous nonwoven nanofibrous substrate faced a series of new challenges as compared to the fabrication of fouling-resistant conventional thin film composites. For example, easy penetration of the coating solution into the more porous nanofibrous substrate is hardly avoided which results in a much thicker barrier layer. In typical

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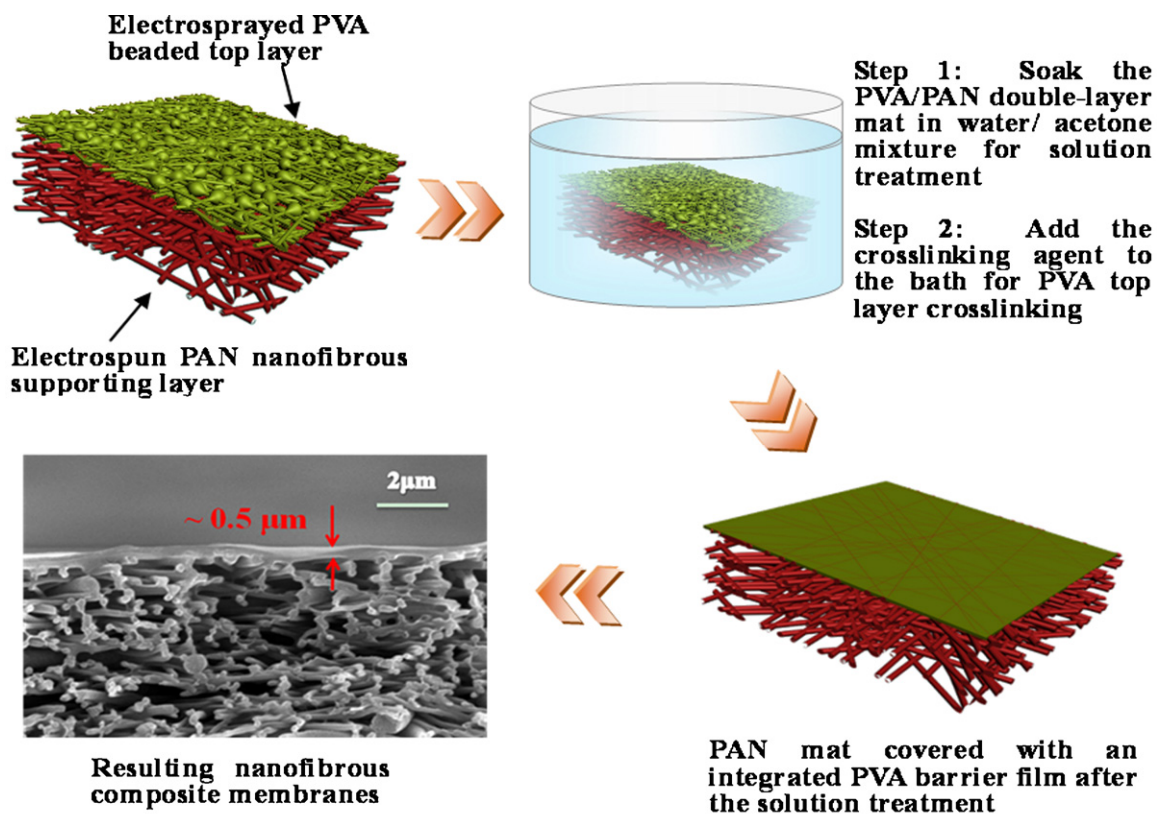


Fig. 1. Schematic illustration of the fabrication process for thin film composite membranes based on PAN nanofibrous substrate and cross-linked PVA barrier layer.

fabrication of surface-coated anti-fouling composite membranes, various methods have been attempted to minimize the penetration of the cast solution to achieve the coating barrier layer as thin as possible. For example, a cast solution with fast gelling time (at room temperature) was used to minimize the penetration [11,14]. A coagulant soaking method was also taken to minimize the penetration of the cast solution into the nanofibrous scaffold [15–17]. Tang et al. [18] reported that a UV-reactive PVA coating could be applied on the nanofibrous scaffold to reduce the penetration. Recently, in our laboratory, we achieved a PVA barrier layer with thickness of 400 nm on electrospun PAN scaffold from a PVA nanofibrous top layer re-melted by water vapor exposure [13].

In this study, we attempted to manufacture a hydrophilic ultra-thin barrier layer on porous nanofibrous nonwoven supporting layer by electro spraying technique combined with solution treatment. For electro spray, small droplets or particles are formed as a result of the varicose breakup of the electrified jet that is often present with a solution of low viscosity [19,20]. The electro spray technique has been widely applied in particle and aerosol development as well as thin film deposition [21,22]. The adjacent particles will be more easily swollen to merge together by suitable solvent penetration. Here, a very thin hydrophilic PVA layer with controlled thickness was first electro sprayed on the PAN nanofibrous nonwoven substrate, then the PVA/PAN double-layer membranes was immersed into suitable solvent water and nonsolvent acetone mixture, the electro sprayed PVA layer will be swollen to merge imperceptibly into an integrated film on the supporting layer during the immersion. Finally, the integrated PVA film layer was chemically crosslinked by glutaraldehyde in water/acetone solution to form a barrier PVA thin layer. Nonsolvent acetone was used to control the swollen degree of PVA. And the water content in the water/acetone solution bath and the immersion time were

optimized to control the beaded PVA top layer be swollen enough to merge imperceptibly into an integrated and nonporous thin PVA barrier layer on the surface of the PAN nanofibrous mat. The filtration performance of the TFNC membranes was evaluated by the separation of oil/water emulsion using a cross-flow device. The mechanical properties of the TFNC membranes were also investigated and discussed.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN, with weight average molecular weight of 1.36×10^5 g/mol) was purchased directly from Shanghai Jinshan Co., Polyvinyl alcohol (PVA, Mw = 146,000–186,000, degree of hydrolysis = 99%) and Triton X-100 were obtained from Aldrich. N,N'-dimethylformamide (DMF), acetone, glutaraldehyde (GA, 25 wt% aqueous solution) and hydrochloric acid (HCl) were kindly supplied by Shanghai Chemical Reagent Plant. Soybean oil was purchased from a local grocery store. DC193 fluid which is a commercial surfactant based on silicone polyether (glycol) copolymer was purchased from Dow Corning.

2.2. Preparation of nonwoven PAN nanofibrous substrate

PAN nanofibrous scaffold was prepared by electro spinning technique in a similar way as described before. In brief, PAN was dissolved in DMF and stirred at 55 °C for 24 h to obtain 8 wt% homogeneous solution. The applied electric voltage was 22 kV and the solution feed rate was 20 μl/min. The spinneret with diameter of 0.7 mm makes a translational oscillatory motion perpendicular to the drum rotation direction (the oscillation distance was about

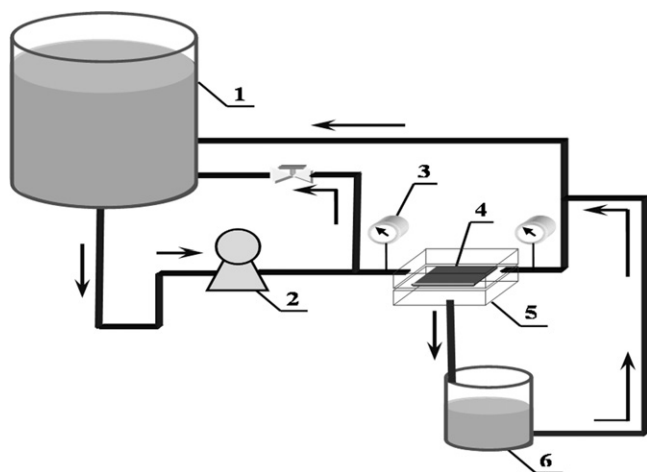


Fig. 2. Schematic illustration of cross-flow filtration setup: (1) feed tank, (2) feed pump, (3) pressure gauge, (4) membrane, (5) membrane cell, and (6) permeate collection tube.

30 cm) driven by a step motor. A grounded rotating metallic drum with diameter of 10 cm, length of 30 cm and rotating speed of 180 rpm was utilized to collect the deposited nanofibers. The distance between the spinneret and the grounded drum was 15 cm. The thickness of the prepared PAN nanofibrous mats is about 100 μm . The electrospun PAN nanofibrous mats acting for supporting layers were cold-pressed at room temperature at 5 MPa for 30 s to improve their mechanical strength and obtain smooth surface for the preparation of PVA barrier layer.

2.3. Preparation of hydrophilic PVA layer by electrospaying

PVA was dissolved in water and stirred at 95 °C for at least 6 h to obtain 1.0–4.0 wt% homogeneous solution for electrospay. When the solution was cooled down to room temperature, Triton X-100 was added into the solution at a concentration of 0.6% (w/v) to reduce the surface tension of the PVA solution. The mixture was stirred further for 15 min before electrospay. The preparation parameters of hydrophilic PVA top layer by electrospay from PVA solution was as follows: the applied electric voltage was 32 kV and the solution feed rate was 15 $\mu\text{l}/\text{min}$. The spinneret diameter was 0.7 mm and the distance between the spinneret and the grounded drum covered with the PAN mat was 20 cm. The thickness of deposited PVA top layer can be adjusted easily by controlling the depositing time.

2.4. Preparation of the TFNC membranes for water filtration

A simple fabrication process was used 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 electrospayed on the surface of PAN nanofibrous substrate to form PVA/PAN double-layer mat. The thickness of the PVA layer can be adjusted easily from several micrometers to tens of micrometers by controlling the depositing time. Secondly, the PVA/PAN double-layer mat was directly immersed into the bath consisting solvent water and nonsolvent acetone. The content of water in the mixture was in the range of 60–80 wt%. Water is the good solvent for PVA and will penetrate into PVA beads, so the PVA top layer would be swollen to merge imperceptibly into a very thin PVA film layer on

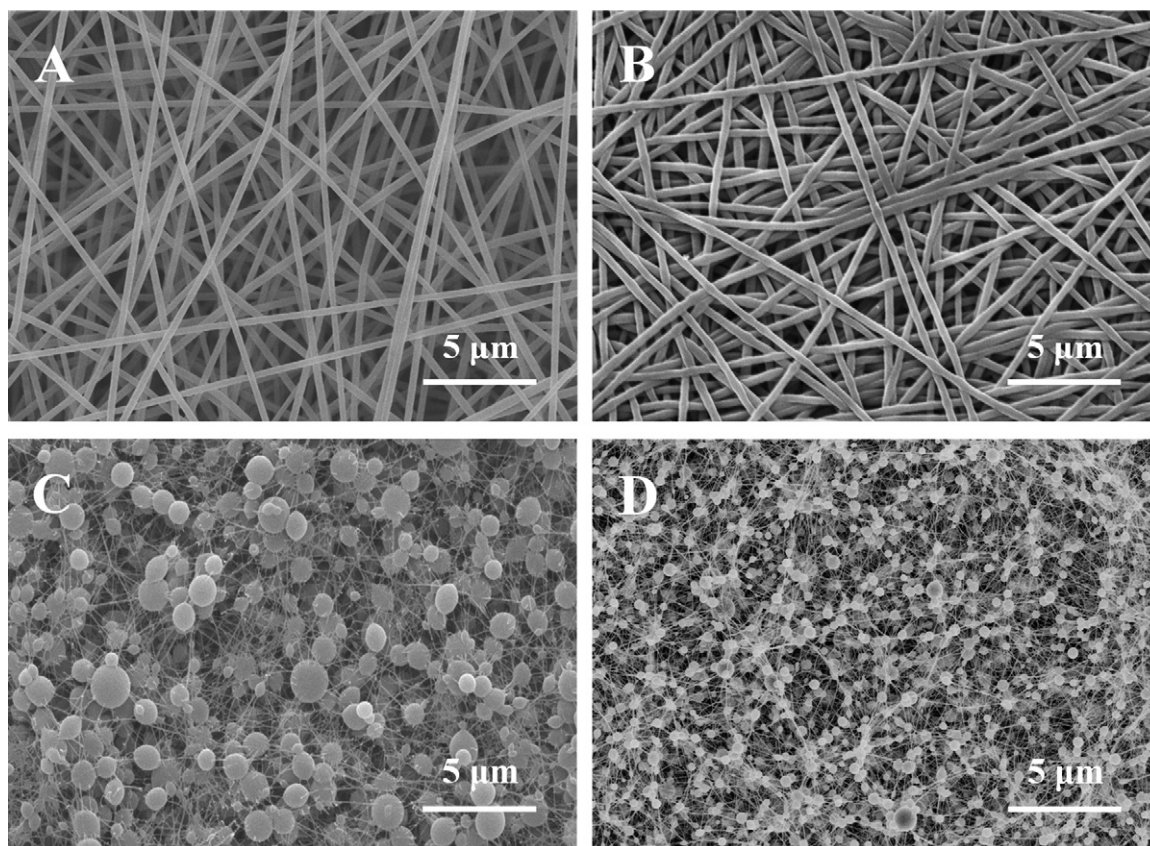


Fig. 3. Typical SEM images of PAN nanofibrous substrate electrospun from 8 wt% PAN/DMF solution before (A) and after (B) cold-pressed at 5 MPa, and electrospayed PVA nanobeads layer from 4.0 wt% PVA aqueous solution (C) and from 1.0 wt% PVA aqueous solution (D).

the surface of the PAN nanofibrous mat. Finally, a given amount of GA was added into the bath, and 1 N HCl solution was used to adjust the pH of the immersion solution at 1.5 to crosslink the PVA film layer for 2 h. The resulting composite membranes were washed with pure water and kept in the water before use.

2.5. Mechanical properties of the PVA/PAN composite membrane

The mechanical properties of the PVA/PAN composite membrane were measured at room temperature by using a Changchun Kexin (Model WDW3020) tensile testing machine. For the tensile test, the gauge length was 30 mm and the narrow width at center was 5 mm. The thickness of specimen was in the range of 70–90 μm . The chosen cross-head speed was 10 mm/min.

2.6. Scanning electron microscopy characterization

The morphology of the samples was investigated by scanning electron microscopy (SEM) (JSM-5600LV, Japan) and analyzed by using image analysis software. The cross-sectioned samples were prepared by fracturing the water-wetted composite membranes in liquid nitrogen.

2.7. Water filtration evaluation

Cross-flow measurements were carried out using oil/water emulsions (soybean oil, 1350 ppm; nonionic surfactant (Dow Corning 193 fluid), 150 ppm in water) at a temperature of 25–30 $^{\circ}\text{C}$. The schematic illustration of cross-flow filtration setup was shown in Fig. 2, and the effective filtration area was 20 cm^2 . Three specimens were filtered for each sample and the quality of filtered water was evaluated by UV–vis spectroscopy based on the absorbance at a wavelength of 230 nm [11].

3. Results and discussion

3.1. Morphology of electrospun PAN and electrospayed PVA

A PAN nanofibrous mat as supporting layer with thickness of ~ 100 nm was manufactured by electrospinning method firstly, then was cold-pressed at room temperature at 5 MPa to improve their mechanical strength and obtain smooth surface for preparing PVA top layer. Fig. 3A and B showed the typical SEM images of the PAN nanofibrous mat before and after cold-pressed. As can be seen, PAN nanofibrous mat showed more compact after being pressed and the morphology of PAN fiber did not change distinctly, the average diameter of the PAN fibers was about 300 nm. For the hydrophilic top layer preparation, a PVA layer enriched with nanobeads was electrospayed on electrospun nanofibrous PAN supporting mat. The representative SEM images of electrospayed PVA layer were shown in Fig. 2C and D. As can be seen, the average diameter of the PVA beads was about 500 nm (Fig. 3C) from 4.0 wt% PVA solution and 250 nm (Fig. 3D) from 1.0 wt% PVA solution, respectively. Although the finer PVA beads will be electrospayed from more dilute PVA solution, it would be take much longer time to obtain a suitable amount of PVA deposit. Here, it should be noted that, the PVA solution with 4.0 wt% will be used for electrospay and the suitable depositing time for PVA electrospay will be set at 60 min in order to form an integrated PVA barrier layer referenced with our previous report [13].

3.2. Optimization of PVA top layer on PAN nanofibrous substrate by solution treatment for the fabrication of TFNC membranes

PVA nanobeads can be dissolved immediately on contact with water. Therefore, when the PVA nanobeads layer was immersed

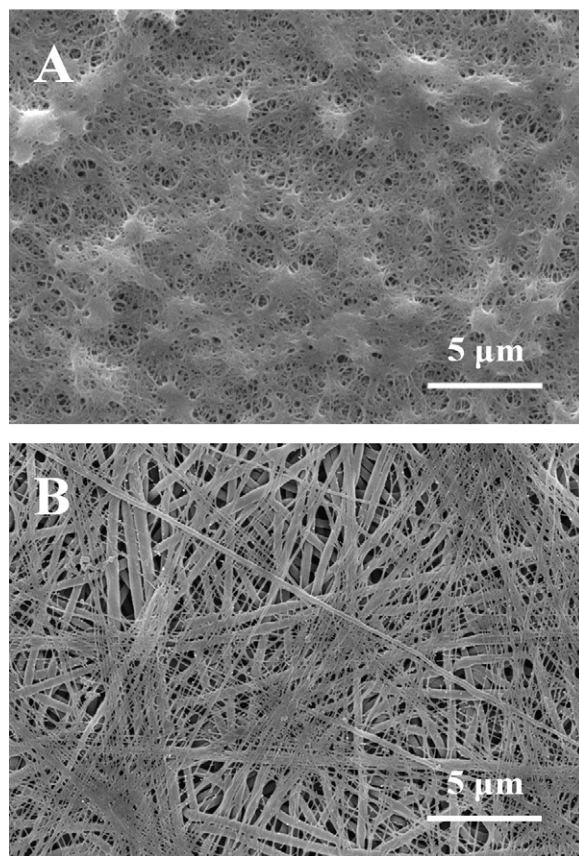


Fig. 4. The surface SEM images of electrospayed PVA top layer with immersion time of 3 h in 60/40 water/acetone solution (A) and 30 min in 80/20 water/acetone solution (B).

into the mixture of solvent water and nonsolvent acetone, the PVA nanobeads would absorb water and be swollen to merge imperceptibly into a thin PVA film layer on the surface of the PAN nanofibrous mat. The nonsolvent acetone was used to control the swollen degree of PVA in solution. The obtained PVA film layer would not be perfect with some pores on surface if the immersion time was too short or too long. The PVA nanobeads would not be swollen sufficiently to spread with short time immersion in the water/acetone solution and PVA nanobeads will be dissolved completely in the bath with long time immersion.

It is obvious that the water concentration of the water/acetone solution is another important factor affecting the morphology and filtration performance of the composite membrane. If the water concentration is too high, the PVA nanobeads would be dissolved too quickly to control, while the PVA nanobeads would not be swollen effectively with low water concentration. For example, PVA nanobeads layer electrospayed from 4% PVA solution cannot be remelted effectively after 3 h when the water concentration of the bath is set at 60 wt% as shown in Fig. 4A. However, the majority of PVA layer could be dissolved into the bath after 30 min (Fig. 4B) if the water concentration is 80 wt%. Thus, the appropriate water concentration for the electrospayed PVA layer was set at 70 wt%, PVA nanobeads layer could be swollen to form an integrated barrier film with suitable immersion time.

For the preparation of PVA/PAN TFNC membranes, electrospayed PVA/PAN double layers were immersed into water/acetone solution for solution immersion with suitable time and then chemically crosslinked by glutaraldehyde in same water/acetone solution for 2 h. The morphology of the top PVA layer could be controlled by adjusting the immersion time of PVA nanobeads. Fig. 4 showed the

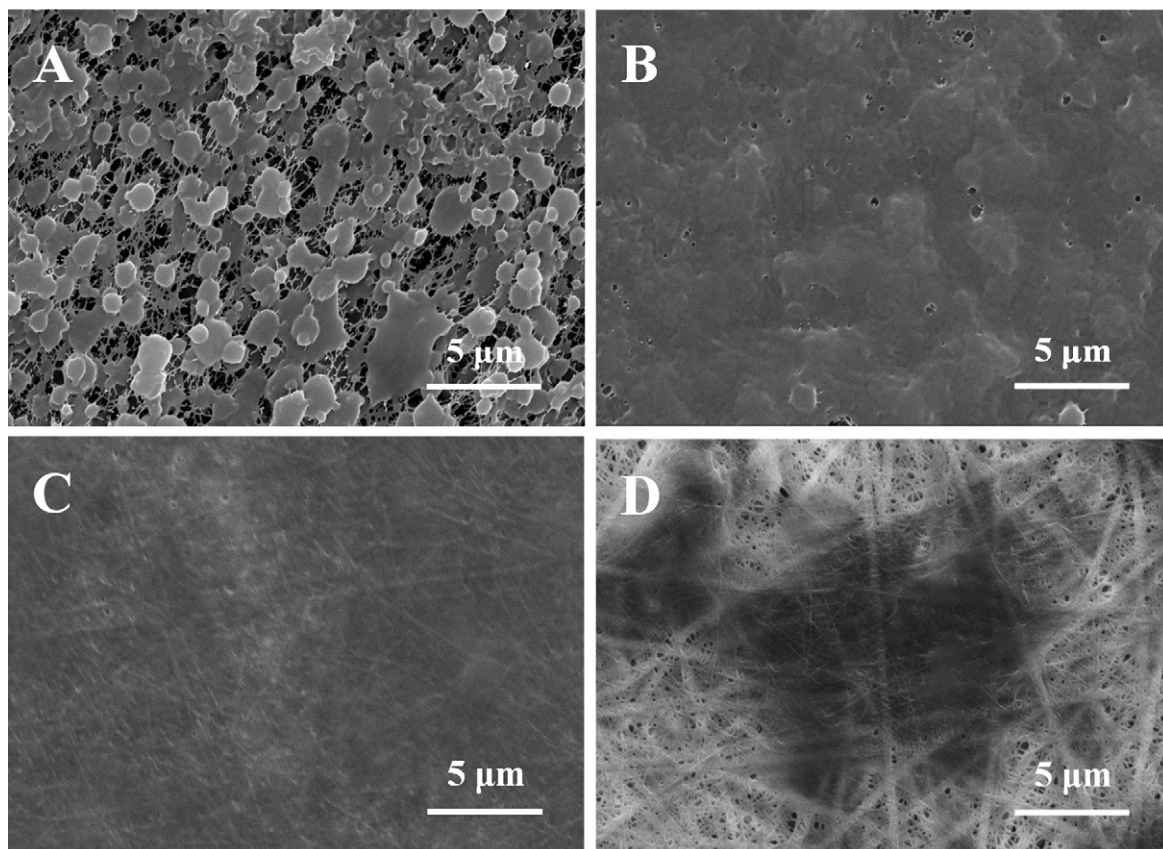


Fig. 5. The surface SEM images of PAN mats covered by cross-linked PVA barrier layer from beaded PVA with different immersion time in 70/30 water/acetone solution: (A, 60 min; B, 90 min; C, 120 min; D, 150 min).

surface SEM images of PAN nanofibrous mats covered by cross-linked PVA barrier layer from PVA beaded layer (PVA/PAN TFNC) with different immersion time. When the beaded PVA/PAN double layer was immersed into the water/acetone solution with the water concentration of 70 wt% for 60 min (as shown in Fig. 5A), the nanobeads of the PVA top layer began to be swollen to merge together imperceptibly, but it is still far away from forming an intact film with short immersion time. With the increase of immersion time to 90 min, the ultra thin PVA top layer was still not perfectly covered on the PAN nanofibrous layer (Fig. 5B), some very small pores were visible. Further increase the immersion time of PVA top layer to 120 min, an integrated PVA barrier layer will be formed on the PAN nanofibrous supporting layer as shown in Fig. 5C. If the immersion time was extended further to 150 min, the PVA barrier layer will be dissolved partially (Fig. 5D).

The typical cross-sectional SEM image of the PVA/PAN TFNC membrane was shown in Fig. 6. As can be seen, the thickness of the PVA barrier layer from electrospun PVA beaded top layer was roughly at $\sim 0.5 \mu\text{m}$.

3.3. Mechanical properties of the composite membranes

The mechanical properties of the PVA/PAN TFNC membranes have been investigated by tensile tests. Fig. 7 showed the tensile stress and strain curves of the electrospun PAN nanofibrous supporting layer before and after cold-pressed (curves A and B), and PVA/PAN TFNC (curve C), respectively. It was obvious that the mechanical properties of electrospun PAN supporting layer were improved significantly by cold-press treatment. As also can be seen, the PVA/PAN composite membrane showed very good overall mechanical strength, the stress–strain curve of the PVA/PAN TFNC

membrane approximated that of the cold-pressed electrospun PAN nanofibrous substrate with the similar elongation at break, and the tensile strength of the composite membrane was just slightly higher than that of the pressed PAN nanofibrous layer. These results were in accordance with our expectation that the electrospun nanofibrous substrate not only provided the interconnected porous structure but also the mechanical strength of TFNC membranes.

3.4. Evaluation of filtration performance of the composite membranes

Cross-flow measurements were performed using oil/water emulsion (soybean oil, 1350 ppm; nonionic surfactant (Dow

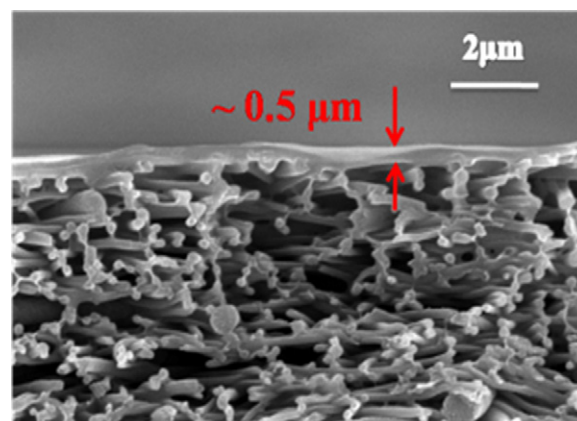


Fig. 6. The typical cross-sectional SEM image of the PVA/PAN TFNC membrane.

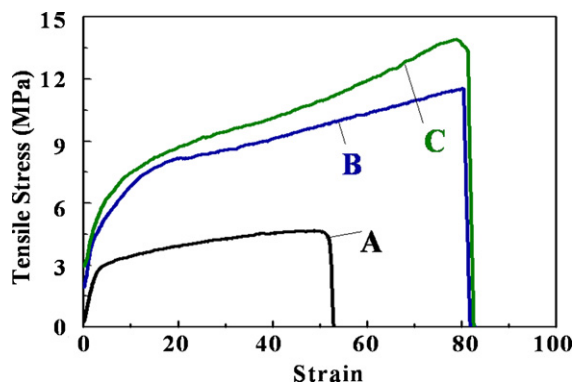


Fig. 7. Stress–strain curves of the electrospun PAN nanofibrous supporting layer before (A) and after cold-pressed (B), PVA/PAN TFNC (C).

Corning 193 fluid), 150 ppm in water) at 25–30 °C to test the ultrafiltration performance of the composite membranes. Fig. 8 illustrated the feeding pressure dependence of the permeate flux of the resulting PVA/PAN TFNC membranes in oily emulsion system by cross-flow filtration. As can be seen, the permeate flux increased with increasing feeding pressure, and the highest flux (419.65 l/m² h) was achieved at the feeding pressure of 0.4 MPa (Fig. 8). The organic rejection of the permeation kept over 99.5% for the PVA/PAN TFNC membranes while the feeding pressure was not higher than 0.4 MPa. If the feeding pressure exceeded 0.4 MPa, the rejection dropped to 95%. These results indicated that the PVA barrier layers on the PAN nanofibrous substrates possessed good mechanical integrity under the feeding pressure range of 0.1–0.4 MPa. The obtained PVA/PAN TFNC membranes here performed reasonably well in terms of providing high water flux with high organic rejection rate as compared with those reported in the literatures at the flux level of ~100 l/m² h [12,18]. Tang et al. [18] demonstrated that the flux rate of the UV cured PVA TFNC membrane was 70.6 l/m² h with high rejection ratio (>99.5%) in oil/water emulsion separation under the operation pressure of 30 psi (0.21 MPa). Correspondingly, the resulting PVA/PAN TFNC membrane possessed much higher flux (347.8 l/m² h) with same organic rejection rate (99.6%) at low feeding pressure (0.2 MPa).

A long-term ultrafiltration with three runs was carried out to further investigate the recycling property of PVA/PAN TFNC composite membranes. Fig. 9 presented the time-dependent flux of PVA/PAN composite membranes for 12 h ultrafiltration at low pressure (0.2 MPa). After three times of oil/water emulsion ultrafiltration with a total operation time of 9 h and corresponding three times of hydraulic cleaning with pure water, the flux of PVA/PAN

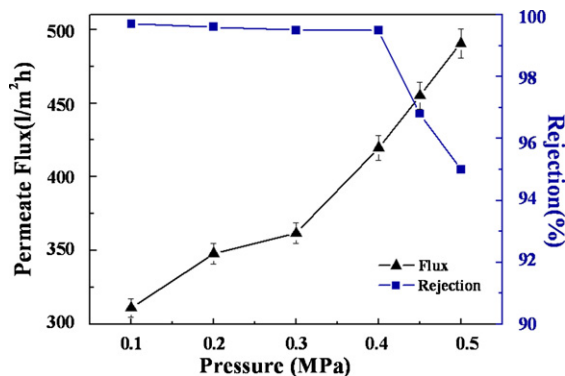


Fig. 8. The pressure dependence of permeate flux and rejection rate of the PVA/PAN TFNC membrane using oil/water emulsion as a feed solution (temperature: 25–30 °C).

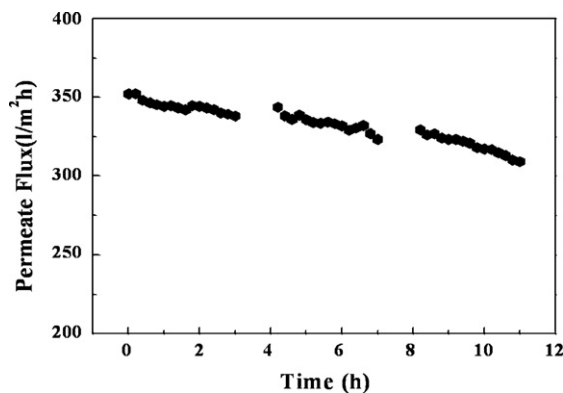


Fig. 9. Time dependence of permeate flux of the PVA/PAN TFNC membrane using oil/water emulsion as a feed solution (temperature: 25–30 °C; 0.2 MPa).

composite membranes maintained at 309.08 l/m² h, 87.8% of the initial value. The steady flux was observed within the experimental time frame without marked fouling. After 12 h filtration treatment, the flux was not reduced significantly compared with the beginning and kept high rejection (>99.5%) all the time. These results indicated that PVA/PAN TFNC membrane has a high flux at low feeding pressure and good anti-fouling property.

4. Conclusions

In summary, a new simple route was developed to fabricate high flux low pressure thin film nanofibrous composite membrane containing a hydrophilic PVA barrier layer and a PAN nanofibrous substrate. The preparation of the hydrophilic PVA barrier layer was accomplished by electrospaying PVA nanobeads on PAN nanofibrous supporting layer followed by solution treatment in water/acetone solution. It was found that the top electrospayed PVA beaded layer could be easily swollen to merge imperceptibly into an integrated film by directly immersing it into the water/acetone solution and chemically crosslinked by adding crosslinking agent (glutaraldehyde) into immersion solution to form a water-insoluble barrier layer on PAN supporting layer. An integrated and nonporous PVA barrier layer could be achieved by adjusting the water content in the water/acetone solution bath and the immersion time. The critical water content in the water/acetone solution bath was found to be 70 wt%. The optimized PVA/PAN composite membranes prepared through this facile route overcame the drawback of easy penetration of the coating solution into the porous substrate in typical fabrication of surface coated composite membranes, and the membranes possessed high flux (347.8 l/m² h) with high rejection rate (99.6%) and good antifouling property in oil/water emulsion separation at very low pressure (0.2 MPa). As can be seen, the method described here for thin film composite membrane preparation is very mild and easily to be handled. Additionally, the nanofibrous composite membranes also showed good overall mechanical properties.

Acknowledgments

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