Preparation and characterization of PES-C/PVPP nanofibrous composite membranes via solution-blowing

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Abstract: In the present paper, PES-C nanofibrous membranes were prepared via solution-blowing technology and the crosslinked-PVP (PVPP) solution was sprayed on the PES-C substrate via homemade solution-blowing apparatus. Then the PVPP was melted and pressed into an integrated barrier film on the supporting layer by hot-pressing treatment. The depositing time of PVPP spray was optimized to achieve an integrated, nonporous PVPP barrier layer. The composite membranes were characterized by scanning electron microscopy (SEM), wide-angle X-ray diffraction (WAXD) and the water contact angles (WCA), etc. Furthermore, the filtration separation experiments of bovine serum albumin (BSA) was executed and antifouling property was measured by comparing the flux recovery ratio (FRR%). The results showed the composite membranes with PVPP-modified possessed an excellent and stability antifouling performances and could be applied in ultrafiltration field.

1. Introduction
As a new type of micron/nanofiber preparation technology, solution-blowing which uses the high-pressure gas stream to form micro/nanofibers has a high efficiency, low cost of the technological equipment in comparison with electrospinning. Solution-blowing is suitable for almost all types of polymers which can be dissolved in common solvent, such as PES, SPEEK, PMMA, PS, PVA, PA-6 and cellulose, etc [1-4]. PES-C which has better thermal stability, tolerance to higher pH and chemical
resistance due to the introduction of cardo groups has been widely used in membrane separation field [5-11]. It is appropriate to prepare PES-C nanofibers via solution-blowing owing to its well solubility in organic solvents. But the poor hydrophilicity of the membrane would lead to serious fouling problem in aqueous solution treatments, as a result, much research has been paid to improve the hydrophobicity of the membrane [12-15]. Among these, PVP as a water-soluble polymer which contains a strong hydrophilic component (the amide group) has been widely used to enhance the hydrophilicity and anti-fouling ability of membranes. However, PVP can leach out during filtration process which would reduce the stability of the modified effect[16]. So there have been many studies about grafting crosslinked-PVP on the surface of membranes by reaction with certain chemical reagent or irradiation with rays [17-19].

In this paper, PES-C with the inherent viscosity $\eta$ of about 0.65 dL/g was dissolved in DMAC to prepare 25 wt% spinning solution. Then its nanofibers were prepared via solution-blowing. PVPP (PVPPK-30 polymerization aqueous with K$_2$S$_2$O$_8$ as initiator system and water as reaction medium) would be sprayed on the surface of the PES-C nanofibrous membrane via homemade solution-blowing (SB) apparatus. The integrated top layer film which was chemically crosslinked was formed through simple hot-pressing treatment. Finally the filtration and antifouling performance of the nascent and composite membranes were evaluated by bovine serum albumin (BSA) water systems.

2. Experimental

2.1. Materials

Bis(4-chlorophenyl) sulfone (DCDPS, 99 %) was purchased from Alfa Aesar.

Sulfolane (99 %) was supplied by ALDRICH (USA) and was purified by active carbon and stored over 0.4 nm molecular sieve.

Phenolphthalein, PVPPK-30 (the average molecular weight is about 40,000 g/mol), Potassium carbonate (K$_2$CO$_3$, 99 %), Potassium persulfate (K$_2$S$_2$O$_8$, 99.5 %) and Bovine serum albumin (BSA) with a molecular weight of ca. 67 k Da were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

N,N-dimethylacetamide (DMAc, 99 %) and Toluene (99.5 %) were acquired from Ling Feng Chemicals Co., Ltd. (Shanghai, China) and was purified by distillation and dried by 0.4nm molecular sieve.

All chemicals were in an analytical grade.

2.2 Membrane Preparation

PES-C with the inherent viscosity $\eta$ of about 0.65 dL/g was prepared ourselves according to the patent[5]. Then the polymer was dissolved in DMAC with the concentration of 25 wt%. After moderate stirring at room temperature for 10 h , the homogeneous solution was left at 25°C for 24 h to remove air bubbles.

A homemade solution-blowing (SB) apparatus was designed to prepare the PES-C nanofibers. The spinning solution was squeezed out through a 0.5 mm inner diameter needle under high-pressure nitrogen. The main spinning parameters was shown below: nitrogen-blowing pressure was 0.1 MPa, solution feeding rate was 4 ml/h, collecting distance was 20 cm. The membranes were dried under vacuum condition at 80°C for 12 h to remove the residual solvent. The thickness of PES-C nanofiber membranes were measured to be about 200 μm, and the apparent density of the membranes were about 18~20 g/m².

The PVPPK-30 and K$_2$S$_2$O$_8$ (weight ratio=1:1) was dissolved in 50 ml deionized water to make a dilute aqueous solution. The concentration of PVPPK-30 was set at 3 wt% and the system temperature was adjusted to 80°C for about 3h [20-21]. Then the PVPP suspension was drawn off with a syringe and left at 25°C for 24 h to remove air bubbles. The main spraying parameters was shown below: nitrogen-blowing pressure was 0.5 MPa, PVPP solution feeding rate was 4 ml/h, collecting distance was 20 cm, the depositing time ranged from 0.5 h to 2 h. After depositing, the composite membranes
were washed with sodium hypochlorite (NaOCl) solution for 10 h to remove the remaining monomer and K2S2O8 [22,23]. After drying, the membranes were heated by two hot plates controlled at 180°C for about 10 min to melt and to be pressed into an integrated layer at about 1 MPa (the PVPP layer down). Then the modified membranes were kept in the water before use. The spraying apparatus was shown Fig 1.

![Schematic of the PVPP-spraying set-up.](image)

2.3 Filtration experiment
A homemade membrane permeation test apparatus was prepared ourselves which contained air pump, gas flow meter and filtering vessel. The PVPP barrier layer was placed upwards. Before the dead-end filtration tests, the membranes were immersed in the deionized water for 30 min to be wetted. The permeation experiments of composite membrane were at 0.05 MPa and the effective membrane area was about 7 cm². The flux was determined by the permeate volume within certain filtration time. The pure water flux (Jw1) was determined by the following equation:

\[
F = \frac{V}{(A \cdot \Delta t)}
\]

Where \(F\) is the membrane flux (L/(m²·h)), \(\Delta t\) is the permeation time (h), \(A\) is the effective membrane area (m²), \(V\) is the volume of permeated water during the time interval (L).

2.4 Antifouling property test
After the pure water flux was examined, BSA solution (1 g BSA in 1 L phosphate buffer) was used as foulant particles to evaluate the antifouling property of PVPP-modified membranes. After 60 min of the protein filtration at 0.05 MPa, the composite membranes were only physically cleaned by tap water for about 10 min, and then the pure water was used to repeat the flux measurement which the flux at 0.05 MPa was examined as Jw2. At least three samples were measured for each type of membrane and the average value was obtained to minimize the test errors. The antifouling property of the membranes was evaluated by flux recovery ratio (FRR%) using the following equation:

\[
\text{FRR}(\%) = \left( \frac{Jw2}{Jw1} \right) \times 100\%
\]

2.5 Characterization
Inherent viscosity \([\eta]\) was measured in DMAc at a concentration of 0.5 g/dL at 25°C using a Ubbelohde viscosimeter.

The morphology of the membranes was examined by scanning electron microscopy (QUANTA 250, Czech Republic).

The average thickness of the nanofibrous membranes was measured using a digital micrometer.

Wide-angle X-ray diffraction (WAXD) was performed on a D8 Advance X-ray diffractometer (Bruker, Germany) with 2θ between 5° and 60°.

Thermogravimetric analysis (TGA) was conducted with a Netzsch TG209F1 Iris instrument carrying out on approximately 5 mg at a heating rate of 10 K/min from 50°C to 800°C under nitrogen
atmosphere at a purge rate of 20 ml/min.

Water contact angle (WCA) measurements were performed using a contact angle goniometer Kino SL200B by the sessile drop method at room temperature. The images were recorded immediately (about 3s) and the mean WCA results were obtained by measuring at least 10 contact angles to get a reliable value.

The BSA concentration of both feed and permeate solutions were measured by a UV–9100 spectrophotometer (LabTech, Beijing) at 280 nm.

3. Results and discussion

3.1 Morphology of membranes

![SEM images](image)

Fig 2. SEM images of different spraying time for thermal treatment (a, 0 h; b, 0.5 h; c, 1 h; d, 1.5 h).

The surface morphology of the original and composite membranes were observed by SEM in Fig 2. It could be seen that the PES-C nanofibers were comparably defect-free and smooth. When the PVPP were sprayed on the surface of the membranes, it would be melted or softened easily through hot-pressing treatment. When the amount of PVPP depositing was enough, it would be formed an ultrathin integrated barrier on the nanofibrous supporting substrates. The result showed that an integrated and smooth film was formed with depositing time of 1.5 h as shown in Fig 1d. If the depositing time was further increased to 2 h, the PVPP barrier would be more thick and become fragile after drying which would deteriorate membranes filtration performance. So the spraying time of 1.5 h was suitable to obtain the PES-C/PVPP composite membrane.

3.2 WAXD analysis of the membranes

The crystal structures of the membranes were analyzed via Wide-angle X-ray diffraction (WAXD) in
Fig 3a. The original PES-C membrane displayed completely amorphous diffraction patterns and showed only one major diffuse diffraction peak at about 18.89° which due to the incorporation of phthalein group. When the PVPP was sprayed on the surface of the membranes (depositing time = 1.5 h), the diffraction peaks increased obviously in intensity and had several diffraction peaks at 2θ that were 24.76°, 27.56°, 37.60°, 46.18° and 51.03° etc. The above results indicated that the crystallinity of composite membranes enhanced while the PVPP top layer was formed on the surface of the membranes.

3.3 The water contact angles of membranes
As we known that the hydrophilicity of the membranes was an important factor to determine their antifouling ability during filtration process. The mean static water contact angles (WCA) were shown in Fig 3b which the membranes were sprayed different time ranging from 0 h to 2 h which corresponding to about 135°, 115°, 85°, 53° and 30° respectively. It could be seen that with the increase of depositing time, more PVPP was immobilized on the surface of the membranes to form an integrated barrier, and WCA decreased obviously from 135° (0 h) to 30° (2 h). The main reason of this phenomenon was the introduction of PVPP which contained strong hydrophilic component (the amide group) and significant hydrophobic moiety (six carbons per monomer unit) with high affinity of water.

3.4 Thermal properties of the membranes
The typical TGA curves of the membranes were summarized in Fig 3c. The result showed that the PES-C nanofibers had excellent stabilities against thermal decomposition which was attributed to the aromatic chains and phthalein groups. The weight loss occurred before 150°C could be attributed to the escape of residual solvent. When the PVPP was deposited on PES-C membranes, it could be observed that the heat resistance of the composite membranes decreased due to the barrier layer. The char yields of the membranes were measured from 46.86 wt% to 32.82 wt% respectively under nitrogen. So the hydrophilic of the composite membranes were greatly enhanced with the decrease of thermal performance.

![Fig 3. The property analysis of the membranes: (a) WAXD of PES-C and PES-C/PVPP membranes; (b) The WCA of the membranes and (c) TGA curves of the membranes with different depositing time, a: 0 h, b: 0.5 h, c: 1 h, d: 1.5 h, e: 2 h.]

3.5 Permeation and antifouling property of the membranes

| Depositing time(h) | Pure water flux (L/(m²·h)) | Recovery water flux (L/(m²·h)) | Flux recovery ratio (%) | Rejection (%) |
|-------------------|---------------------------|-------------------------------|------------------------|--------------|
| 0                 | 1400 ± 145                | 1335 ± 88                     | 95.4 ± 8.6             | <1           |
| 0.5               | 720.5 ± 69                | 631.2 ± 47                    | 87.6 ± 6.5             | 4.26 ± 0.6   |
| 1                 | 477.7 ± 45                | 398.1 ± 35                    | 83.3 ± 7.3             | 17.44 ± 2.8  |
| 1.5               | 409.5 ± 21                | 307.2 ± 16                    | 75.1 ± 4.1             | 75.88 ± 5.1  |
| 2                 | 380.2 ± 18                | 305.3 ± 15                    | 80.3 ± 2.2             | 76.11 ± 4.3  |
A dead-end filtration system was carried out to characterize the separation and filtration performance of the membranes. Bovine serum albumin (BSA) was selected as a model protein to investigate the antifouling performance. The filtration parameters of the membranes were shown in Table 1. The pure and recovery water flux of PES-C membrane, PES-C/PVPP composite membranes with depositing time of 0.5 h and 1 h were measured at ambient pressure, while the depositing time of 1.5 h and 2 h were measured at 0.05 MPa. The pore size of PES-C nanofibrous membrane was micron scale, so the pure water flux was about 1400 L/(m²·h) under gravity, and the rejection of the BSA was less than 1 % which meant nearly all the particles had passed through the membrane. So the standard filtration model (BSA) was not suitable for analyzing the fouling mechanisms of PES-C nanofibrous membrane, because the size of particles was too smaller compared to the membrane pore size. With the increase of spraying time (2 h), protein rejection coefficient increased to about 76.11 % while the pure water flux (Jw1) decreased to about 380.2 L/(m²·h). The flux recovery ratio (FRR%) was above 75 % owing to the introduction of PVPP which enhanced the interaction with water. The adsorbed protein on the membranes surface could be removed by water flushing. The rejection coefficient would continue to raise with increase thickness of PVPP layer, but the surface of modified membranes would become brittle and crack easily due to the thick layer. In general, the PVPP depositing time of 1.5 h would be a relatively suitable parameter to form an ideal composite membrane.

4. Conclusions
In this paper, PES-C was dissolved in DMAc to prepare 25 wt% spinning solution and the nanofibers were prepared via solution-blowing technology. Then PVPP solution was sprayed on the surface of the membrane to form an integrated barrier layer by simple hot-pressing treatment. The different depositing time was discussed and 1.5 h was considered as appropriate time to obtain the composite membrane. Then the filtration experiments of BSA solution were executed to evaluate the property of the membranes. The membranes with depositing time of 1.5 h possessed BSA rejection rate of about 75% and the flux recovery ratio of above 75%. How to further optimize its nanofiltration performance would be our next work.

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