Novel gelatin/polyacrylonitrile thin film nanofibrous composite membranes with high filtration performance

Ke Shen, Xuefen Wang*
State Key Lab for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai, 201620, P.R. China
wangxf@dhu.edu.cn

Abstract: High performance thin film nanofibrous composite (TFNC) membrane consisting of a thin gelatin (GE) selective skin layer and a polyacrylonitrile (PAN) nanofibrous substrate was fabricated in this work. Ultrathin GE nanofibers were electrospun and deposited onto the PAN nanofibrous supporting membranes and followed by moistening treatment and hot-pressing treatment. The moistened electrospun GE nanofibers would be melted and pressed into an integrated selective skin layer on the porous PAN nanofibrous membranes. The treated GE/PAN double-layer membranes were then chemically cross-linked by glutaraldehyde (GA). The depositing time of GE nanofibers was optimized to achieve a thin and integrated GE separating layer. The optimized GE/PAN TFNC membrane exhibited high flux (182.1 L m$^{-2}$ h$^{-1}$) and rejection (98.3%) in BSA test at 0.3 MPa. In addition, the GE/PAN composite membrane possessed great mechanical stabilities.

1. Introduction
Recently, the freshwater shortage has been a pervasive and formidable challenge that mankind must be confronted through the word, and the emissions of industrial wastewater is further increasing this threat[1-3]. Membrane separation technology is one of the important technologies for the preparation of fresh water. High permeate flux and rejection are the main purposes of membrane preparation. In order to improve the membrane separation performance, membranes with hierarchical structures have attracted much attention in the field of water purification because of their enhanced filtration efficiency and great mechanical stabilities.

The composite membranes usually consist of a thin separating layer and a porous supporting mat. The conventional supporting substrate is an asymmetric and compact membrane prepared via phase inversion technology affording enough mechanical strength. Recently, the electrospun nanofibrous substrate has received great attention due to its interconnectivity, huge specific surface area and porosity. The thin separating skin layer is commonly fabricated by interfacial polymerization (IP)[4], surface coating[5] and layer-by-layer self-assembly[6]. In particular, surface coating is a right common method for the fabrication of selective skin layer. However, the coating solution is easy to penetrate into the porous nanofibrous mat, which reduces the permeation flux of the TFNC membrane. Recently, various approaches have also been developed to reduce the penetration of the coating solution, such as introducing a hydrophilic interlayer[7, 8], swelling the functional nanofibrous layers by solvent vapor or solution treatment[9].

In this work, inspired by the electrostatic powder coating technique, a simple way was proposed to prepare the composite membrane by melting and hot-pressing the GE nanofibers to form an thin and integrated separating skin layer on the porous PAN mats. Considering the intermolecular hydrogen
bonds of GE molecules, we used water as a plasticizer to promote the GE nanofibers melting. The depositing time of GE nanofibers was optimized to achieve a defect-free GE separating skin layer. The final GE skin layer was chemically cross-linked by glutaraldehyde (GA) and the separation performance of the obtained GE/PAN TFNC membrane was tested by BSA water solution.

2. Experimental

2.1. Materials

PAN (M<sub>w</sub>=150 kDa) and BSA (M<sub>w</sub>=67 kDa) were purchased from J&K Scientific Ltd. Gelatin (GE) from porcine skin and Triton X-100 were purchased from Sigma-Aldrich. Glutaraldehyde (GA, 25wt% in aqueous solution), acetone and N, N′-dimethylformamide (DMF) were supplied by Shanghai Chemical Reagent Plant. All the above reagents were of analytical grade.

2.2. Preparation of GE/PAN TFNC membrane

The fabrication of PAN nanofibrous supporting membrane has been reported in our studies[10, 11]. The prepared PAN nanofibrous supporting membranes (8 cm×8 cm) were pressed at 5 MPa for 25 s to enhance the mechanical strength and provide a relatively smooth surface for the following fabrication of GE separating layer. The purified GE was dissolved in acetic acid aqueous solution (the mass ratio of acetic acid to water was 1:4) to prepare a 25 wt% GE spinning solution. The feeding rate of the GE acetic acid aqueous solution was 5 μL/min. The applied voltage was 28 kV. The experimental temperature for electrospun was at 25 °C. The deposition time of GE layer onto the PAN substrate was 0, 20, 40, 60 and 80 min respectively. Then, the GE/PAN double-layer nanofibrous membranes were moistened in a enclosed environment (the humidity of the environment was maintained by saturated potassium sulfate solution, 98%) for 1 h. The moistened GE/PAN membranes were pressed by two metal plates (the plate temperature was maintained at 50 ℃) under the weight pressure 0.02 MPa. Finally, the fabricated GE/PAN membranes were cross-linked by 0.15 M GA in acetone solution (the pH of acetone solution was adjusted to 1.5 by HCl solution) for 1 h. The final TFNC membranes were washed with DI water and kept in DI water for the following tests.

2.3. Characterization

The morphologies of the composite membrane surfaces and cross-sections were characterized by scanning electron microscope (SEM). Before the observation of the cross-section structures, the water-wetted TFNC membranes were fractured in liquid nitrogen.

The mechanical properties of PAN electrospun membrane, GE/PAN double-layer nanofibrous membrane and cross-linked GE/PAN composite membrane were tested by a tensile testing machine (Model WDW3020, China).

2.4. Membrane filtration evaluation

Filtration performance of the prepared TFNC membrane was tested by a dead-end filtration device. The feeding solution was 100 ppm BSA. Before the test, the samples were pre-pressed at 0.4 MPa for 30 min. Then the TFNC membranes were tested at 0.3 MPa by BSA solution. In order to ensure the accuracy of NF performance, five samples were tested to obtain the final results. The water flux was defined as follows:

\[ F = \frac{V}{A \cdot t} \]  \hspace{1cm} (1)

where \( V \) is the volume of the penetrated solution, \( A \) is the filtration membrane area, and \( t \) is the nanofiltration time.

The solute rejection was defined as follows:
\[ R = (1 - \frac{C_p}{C_f}) \cdot 100\% \] (2)

where \( C_p \) is the contents of BSA in the permeated solution and \( C_f \) is the contents of BSA in the feeding solution. The BSA concentration was detected by using an ultraviolet (UV) spectroscopy (TU1950, China).

3. Results and discussion

3.1. Morphology of electrospun PAN and GE

PAN nanofibrous substrate was fabricated by electrospinning, and cold-pressed at 5 MPa for 25 s at room temperature to provide smooth surface for the subsequent construction of GE skin layer. Figure 1a shows the SEM image of the PAN membrane surface after cold-pressing. The mean diameter of PAN nanofibers was approximately 275 nm, which was calculated from the image processing software (Nano Measure). For the preparation of complete GE selective skin layer, superfine GE nanofibers were electrospun onto the PAN porous mats. The SEM images of the electrospun GE layer was presented in figure 1c. The mean diameter of the GE nanofibers was approximately 107 nm. Here, the amount of the GE nanofibrous layer could be controlled by its depositing time.

![Figure 1. SEM images and fiber diameter with its distribution of (a, b) PAN nanofibrous membranes and (c, d) GE nanofibrous membranes.](image)

3.2. Optimization of barrier skin layer by GE depositing time

Inspired by the electrostatic powder coating technique, the ultrathin electrospun GE nanofibers were moistened in a enclosed environment and then hot-pressed by two metal plates to form an defected-free selective skin layer on the PAN nanofibrous mat. The influence of the depositing time on the formation of ultrathin GE functional skin layer was studied under fixed condition (moistcuring time, 1 h, heating temperature, 50 ℃, hot-press time 1 min). Figure 2 showed the surface morphology of the GE skin layer fabricated with different depositing time of GE electrospun. When the GE nanofiber depositing time was short, the melt GE layer was not enough to cover the underlying PAN supporting membranes. As the depositing time raised to 80 min, an intact GE layer could be prepared after hot-press treatment. With further increase of the GE nanofiber depositing time, the obtained GE skin layer would become thicker, which may reduce the water flux. Thus, the GE layer depositing time for the TFNC membrane preparation was fixed at 80 min for the mechanical strength test and the filtration performance test.
Figure 2. The SEM images of membrane surfaces with different GE nanofiber depositing times (a, 0 min; b, 20 min; c, 40 min; d, 60 min; e, 80 min). (f) The section SEM image of membrane with 80 min GE nanofibers deposition.

3.3. Mechanical properties of the TFNC membranes
The mechanical strengths of the PAN supporting membrane, GE/PAN double-layer nanofibrous membrane and the cross-linked GE/PAN TFNC membrane (the GE depositing time was 80 min) were compared in the figure 3. The tensile strength of the PAN supporting membrane was 12.9 MPa. After the deposition of 80 min GE nanofibers, the GE/PAN double-layer nanofibrous membrane processed an increased tensile strength of 18.3 MPa. The hot-pressed and cross-linked GE/PAN TFNC membrane showed the highest mechanical property of 22.5 MPa, which exhibited that the fabricated TFNC membranes had satisfactory mechanical strength for practical applications.

Figure 3. Tensile stress-strain curves of the PAN supporting membrane, GE/PAN double-layer nanofibrous membrane and cross-linked GE/PAN TFNC membrane.

3.4. Filtration performance of the TFNC membranes
The separation performance of the composite membrane was investigated by a dead-end filtration device with 100 ppm BSA solution at 0.3 MPa. Figure 4 showed the relations of the filtration performance varied with different GE layer deposition times. As the GE layer depositing times increased from 0 min to 80 min, the water permeate flux of the composite membranes decreased from 5100.0 L m⁻² h⁻¹ to 182.1 L m⁻² h⁻¹, while the BSA rejection of the composite membranes enhanced from 3.0% to 98.3%. 

Figure 4. The relations of the filtration performance varied with different GE layer deposition times.
Figure 4. The (a) water flux and (b) BSA rejection rates of the GE/PAN composite membranes prepared with different GE nanofiber deposition times (0.3 MPa, 100 mg/L BSA solution).

Figure 5. The (a) pressure dependence and (b) time dependence of the flux and rejection of composite membrane using BSA solution. (the GE deposition time was 80 min).

We further evaluated the effect of the operating pressure on the separation performance of the TFNC membrane prepared with 80 min GE nanofibers deposition. Figure 5a showed that the permeate flux of the obtained composite membrane were increased linearly simultaneously with the raise of the operating pressure, and the BSA rejection maintained a high level. The fluxes of the TFNC membranes enhanced from 63.1 L m⁻² h⁻¹ to 281.2 L m⁻² h⁻¹ under the investigated operating pressure from 0.1 to 0.5 MPa. Thus, the composite membrane had great mechanical stability under the tested operation pressure. A long-term filtration test with three runs was carried out to further estimate the anti-fouling property of the TFNC membrane for 18 h (100 ppm BAS solution, 0.3 MPa). The permeate flux of the three runs reduced slowly while the BSA rejection maintained over 98.1% during the long-term filtration test, which demonstrated the good stability and anti-fouling property of the resultant membrane.

4. Conclusion
In this work, a GE/PAN TFNC membrane was successfully prepared by electrospinning technique and hot-press treatment. The GE selective layer was prepared by electrospinning GE nanofibers onto PAN nanofibrous substrate, followed by hot-press treatment assisted by moisture absorption. When the deposition time of GE layer was 80 min, a defect-free GE skin layer was obtained for filtration test. The optimized TFNC membrane exhibited the high flux (182.1 L m⁻² h⁻¹) and rejection (98.3%) for 100 ppm BSA solution under 0.3 MPa. It is believed that the strategy in this work can be extended to different polymeric materials for membrane separating process.

Acknowledgments
This work was supported by Shanghai Natural Science Foundation (19ZR1401300) and the Program for Innovative Research Team in University of Ministry of Education of China (IRT_16R13).
Notes and references

[1] Solomon M.F.J., Bhole Y., Livingston A.G. (2013) High flux hydrophobic membranes for organic solvent nanofiltration (OSN)—Interfacial polymerization, surface modification and solvent activation. J. Membr. Sci., 434: 193-203.

[2] Huang L., Chen J., Gao T., Zhang M., Li Y., Dai L., Qu L., Shi G. (2016) Reduced graphene oxide membranes for ultrafast organic solvent nanofiltration. Adv. Mater., 28: 8669-8674.

[3] Shen L., Cheng C., Yu X., Yang Y., Wang X., Zhu M., Hsiao B.S. (2016) Low pressure UV-cured CS–PEO–PTEGDMA/PAN thin film nanofibrous composite nanofiltration membranes for anionic dye separation. J. Mater. Chem. A, 4: 15575-15588.

[4] Gong G., Wang P., Zhou Z., Hu Y. (2019) New insights into the role of an interlayer for the fabrication of highly selective and permeable thin-film composite nanofiltration membrane. ACS Appl. Mater. Interfaces, 11: 7349-7356.

[5] Shen L., Yu X., Cheng C., Song C., Wang X., Zhu M., Hsiao B.S. (2016) High filtration performance thin film nanofibrous composite membrane prepared by electrospaying technique and hot-pressing treatment. J. Membr. Sci., 499: 470-479.

[6] Cao M., Zhao W., Wang L., Li R., Gong H., Zhang Y., Xu H., Lu J. (2018) Graphene Oxide-Assisted Accumulation and Layer-by-Layer Assembly of Antibacterial Peptide for Sustained Release Applications. ACS Appl. Mater. Interfaces, 10: 23937-24946.

[7] Wang J., Yang H., Wu M., Zhang X., Xu Z. (2017) Nanofiltration membranes with cellulose nanocrystals as an interlayer for unprecedented performance. J. Mater. Chem. A, 5: 16289-16295.

[8] Karan S., Jiang Z., Livingston A.G. (2015) Sub–10 nm polyamide nanofilms with ultrafast solvent transport for molecular separation. Science, 348: 1347-1351.

[9] You H., Yang Y., Li X., Zhang K., Wang X., Zhu M., Hsiao B.S. (2012) Low pressure high flux thin film nanofibrous composite membranes prepared by electrospaying technique combined with solution treatment. J. Membr. Sci., 394: 241-247.

[10] Yang Y., Li X., Shen L., Wang X., Hsiao B.S. (2017) A durable thin-film nanofibrous composite nanofiltration membrane prepared by interfacial polymerization on a double-layer nanofibrous scaffold. RSC Adv., 7: 18001-18013.

[11] Shen K., Cheng C., Zhang T., Wang X. (2019) High performance polyamide composite nanofiltration membranes via reverse interfacial polymerization with the synergistic interaction of gelatin interlayer and trimesoyl chloride. J. Membr. Sci., 588: 117192.