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Preparation and Characterization of Multi-layer Poly(arylene sulfide sulfone) Nanofibers Membranes for Liquid Filtration

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Electronic Supplementary Information

Abstract Owing to the excellent filtration performance and low energy cost, polymeric nanofibers microfiltration (MF) membranes have attracted increasing attentions. Poly(arylene sulfide sulfone) (PASS), as one of the structurally modified polymers based on poly(phenylene sulfide) (PPS), has been selected as the raw material to fabricate nanofibers MF membranes *via* electrospun techniques. The effects of PASS solution and the electrospinning processing parameters on the structural morphology of nanofibers were investigated in detail. The average diameter of PASS nanofibers was (296 ± 46) nm under the optimal condition: polymer concentration of $0.27 \text{ g} \cdot \text{mL}^{-1}$ PASS/DMI, applied voltage of 20 kV, and speed of collector drum of $300 \text{ r} \cdot \text{min}^{-1}$. And then the multi-layer PASS nanofibers MF membranes were fabricated from cold-pressing the optimized PASS nanofibers (as-prepared PASS nanofibers) membrane. The morphology, porosity, pore size, mechanical properties, and surface wettability of the multi-layer PASS nanofibers MF membranes could be tuned by the layers of as-prepared nanofibers membrane. The results demonstrated that the membrane with 6 layers (marked as PASS-6) exhibited the smallest porosity, smallest pore size, highest mechanical property, and best surface wettability. Meanwhile, the multi-layer PASS nanofibers MF membranes showed that the rejection ratio gradually increased, while the pure water flux decreased with increasing membranes thickness. The PASS-6 membrane exhibited large water flux of $747.76 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ and high separation efficiency of 99.9% to $0.2 \mu\text{m}$ particles, making it a promising candidate for microfilter.

Keywords Poly(arylene sulfide sulfone); Electrospinning; Nanofibers membranes; Microfiltration

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INTRODUCTION

The inherent advantages of polymeric filtration membranes such as easy fabrication, relatively low operating temperature, low energy consumption, and cost-effectiveness have made them prominent candidates for wastewater purification.^[1–3] Filtration membranes can be divided into four major classes according to the pore size: microfiltration, ultrafiltration, nanofiltration, and reverse osmosis.^[4–7] Among them, microfiltration (MF) membranes, with pore sizes ranging from $0.1 \mu\text{m}$ to $10 \mu\text{m}$, have drawn growing attention to the pretreatment of sewage or removal of fine particles or bacteria.^[8,9]

Conventional polymeric membrane materials include poly(vinylidene difluoride) (PVDF),^[2] poly(acrylonitrile) (PAN),^[3] poly(ethersulfone) (PES),^[8] poly(vinyl alcohol) (PVA),^[9] and polypropylene (PP).^[10] To meet the requirements of practical applications, many new kinds of poly-

meric membrane materials have been exploited.^[4,5,7] Poly(arylene sulfide sulfone) (PASS) is a novel high-performance polymer resin and develops rapidly in recent years.^[11,12] More importantly, this polymer is capable of satisfying the requirement of filtration membrane in harsh application environment because of its prominent thermal stability and solvent resistance.^[13,14] It has been proved that PASS membranes can be widely applied in microfiltration, ultrafiltration, and nanofiltration even in the presence of corrosive organic solvents.^[15–17] However, PASS MF membranes, fabricated by phase inversion, have a common drawback of low flux that most of porous flat polymeric membranes are facing. Fortunately, electrospun nanofibers membranes can address this problem because of the tiny diameter, high surface-to-volume ratio, large porosity, and continuously interconnected pores.^[8,9] For instance, Liu *et al.*^[9] indicated that electrospun poly(vinyl alcohol) (PVA) membrane can achieve 1.5–6 times higher water flux than that of the $0.22 \mu\text{m}$ commercial Millipore microfiltration membrane. Wang *et al.*^[18] reported that electrospun polyacrylonitrile (PAN) nanofibers membranes exhibit significantly high flux varied from $15890 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ to $487 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$. To date, though

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quantities of polymeric materials have been applied to prepare electrospun nanofibers membranes,^[8–10,19] to our knowledge, PASS nanofibers have never been employed as filtration materials. So, it is meaningful to prepare a PASS nanofibers microfiltration membrane with high water flux.

As a majority of waterborne micron-sized particles have sizes larger than 0.2 μm ,^[18,20] it is necessary for MF membranes to possess a high rejection ratio for 0.2 μm particles. The MF membranes with smaller pore sizes would exhibit better rejection rate toward above particles.^[21] Ma *et al.*^[22] found that the mean pore size of nanofibers membrane was about (3 ± 1) times the mean fiber diameter, and Wang *et al.*^[18] demonstrated that the membrane pore sizes decreased with the fall of membrane porosity. Thus, the pore sizes of electrospun membranes are directly related to nanofiber diameter and membrane porosity.^[9,22,23] In other words, the pore sizes of nanofibers membranes could be regulated by tuning the nanofiber diameter and/or the membrane porosity. As a result, electrospun nanofibers MF membranes can surely be prepared with various pore sizes to meet different filtration needs.

The target of the present research is to prepare PASS nanofibers MF membranes with high water flux and high rejection rate to contaminants with sizes no less than 0.2 μm . In this study, electrospun PASS nanofibers membranes with suitable size were prepared at room temperature for the first time. Then the influences of processing parameters and polymer concentrations exerted on the morphology and diameter of fibers were investigated systematically. Moreover, the pore sizes of nanofibers membranes were further adjusted through cold-pressing as-prepared nanofibers membrane into multiple layers. The morphology, porosity, pore sizes, and mechanical properties of the obtained multi-layer PASS nanofibers membranes were characterized by scanning electron microscopy (SEM), capillary flow porometry, and electronic universal testing, respectively. Furthermore, water contact angle, pure water flux, and rejection ratio were thoroughly investigated to evaluate the microfiltration performance of multi-layer PASS nanofibers membranes.

EXPERIMENTAL

Materials

Poly(arylene sulfide sulfone) (PASS) with $[\eta] = 0.56 \text{ dL} \cdot \text{g}^{-1}$ was synthesized in our own laboratory.^[11] 1,3-Dimethyl-2-imidazolidinone (DMI) was provided by Shandong Binzhou

Yuneng Chemical Co., Ltd. (China) and used as received. Lumisphere uniform fluorescent polystyrene (PS) microparticles (0.2 and 0.5 μm) were obtained from Tianjin Baseline Chromatographic Technology Co. (China). Deionized water used throughout the experiment was laboratory homemade.

Preparation of Multi-layer PASS Nanofibers Membranes

Electrospinning of as-prepared PASS nanofibers

PASS was dissolved in DMI and stirred at 170 $^{\circ}\text{C}$ for 6 h to obtain a homogeneous solution. PASS solutions with various concentrations in the range of 0.20–0.27 $\text{g} \cdot \text{mL}^{-1}$ were then prepared. The operating voltage, ranging from 15 kV to 25 kV, was provided by a direct current high voltage power supply (ZGF Chuan Gao electro-tech Inc, China). During the electrospun process, PASS solution was first placed in a 50-mL syringe, to which was attached a needle tip of 0.7 mm inner diameter. The positive electrode was connected to the needle and the distance between the needle tip and the collector was maintained at 20 cm. Then randomly oriented nanofibers were electrospun onto a piece of aluminum foil. The speed of grounded rotating drum which was used as a collector varied from 100 $\text{r} \cdot \text{min}^{-1}$ to 300 $\text{r} \cdot \text{min}^{-1}$. The experimental environmental temperature was around 25 $^{\circ}\text{C}$, with relative humidity ranging from 71% to 76%.

Preparation of multi-layer PASS nanofibers membranes

The nanofibers membranes prepared under the optimal electrospun condition, called as-prepared PASS membrane, was dried in a vacuum oven at 60 $^{\circ}\text{C}$ overnight to completely remove the residual solvent. To improve the mean surface pore size and mechanical strength, the dry PASS membranes were pressed between two flat metal plates using a pressing machine (SHR-10A, Chengdu Hangfa Hydraulic Engineering Co., Ltd.) at room temperature under pressure of 2.5–12.5 MPa for 5 min.

Through the above cold-press procedure of the as-prepared PASS membrane, the optimized pressure for nanofibers membranes was obtained. Then, multi-layer PASS nanofibers membranes were prepared under the same condition. The schematic diagram of multi-layer PASS nanofibers membranes is presented in Fig. 1. Four kinds of membranes (1, 2, 3, and 6 layers) prepared by cold-pressing as-prepared PASS nanofibers membrane were denoted as PASS- x , where x represents the layers of overlaid membranes.

Characterizations

Scanning electron microscopy (SEM, Inspector F, FEI Company) was used to observe the surface and cross-

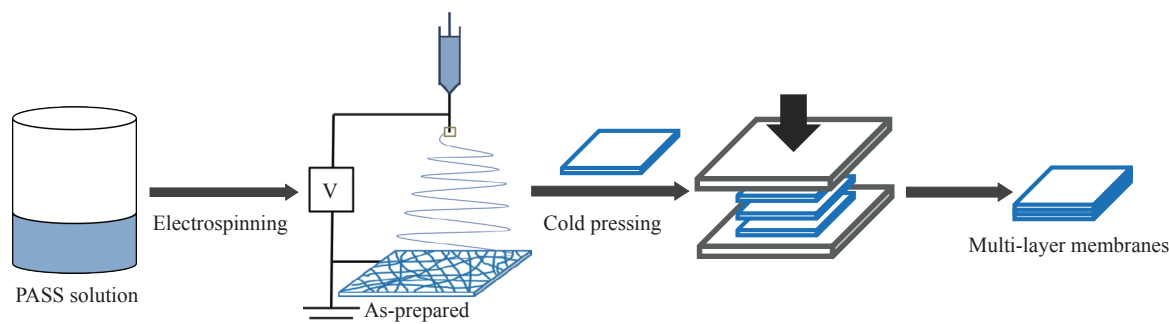


Fig. 1 Schematic diagram for the preparation of multi-layer PASS nanofibers membranes

sectional morphologies of the electrospun PASS nanofibers. The average diameter of nanofibers was measured by analyzing the SEM images with a Image J software and 110 fibers were selected for each case.

Membrane porosity (P_r) was obtained by a gravimetric analysis method. The porosity (P_r , %) of the nanofibers membranes was calculated by Eq. (1):

$$P_r(\%) = \left(\frac{W_1 - W_0}{A d \rho} \right) \times 100 \quad (1)$$

where W_1 is the weight of the wet membrane (g), W_0 is the weight of the dry membrane (g), A is the area of PASS membrane (cm^2), d is the thickness of membrane (cm), and ρ is the density of deionized water ($1 \text{ g}\cdot\text{cm}^{-3}$). A digital micrometer was used to obtain the thickness of the multi-layer PASS nanofibers membranes. The mean pore size distribution of the prepared MF membranes was estimated by using a capillary flow porometer (Porolux 1000, Porometer).

Mechanical properties were evaluated on a universal material testing machine (Instron 5967). The size of the specimens was $8 \text{ mm} \times 50 \text{ mm}$ and the tensile speed was $10 \text{ mm}\cdot\text{min}^{-1}$.

Water contact angle of nanofibers membranes was measured by a video optical contact angle system (Kruss, DSA100, Hamburg, Germany) at ambient temperature.

Microfiltration Performance Evaluation

Pure water flux

The pure water flux was measured with a dead-end filtration device with the effective testing zone of 10.75 cm^2 for each sample. PASS membrane was pre-washed under the pressure over 0.1 MPa for 30 min to completely expel residual air bubbles and open all pores. Pure water flux experiment in this study was carried out under 0.1 MPa . The flux (J , $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) of the nanofibers membranes was determined according Eq. (2):

$$J = \frac{V}{A \times t} \quad (2)$$

where V is the volume of permeate water (L), t is the separation time for flux test (h), and A is the effective filtration area (m^2).

Rejection rate

The rejection performance of PASS membranes was evaluated after water flux measurement. The PS particle suspensions with a diameter of 0.2 or $0.5 \text{ }\mu\text{m}$ was diluted in deionized water to prepare the feed solution of 100 ppm . The concentrations of PS microspheres suspensions were detected by a UV-Vis spectrophotometer (Shanghai TECHCOMP, UV-2310II, China) at 229 and 233 nm , respectively. The percentage of particles rejection was calculated with the following Eq. (3):

$$\text{Rejection}(\%) = \left(\frac{c_f - c_p}{c_f} \right) \times 100 \quad (3)$$

where c_f and c_p are the PS particles concentrations in the feed solution and permeate solution, respectively.

Antifouling tests

For the antifouling performance analysis, $0.2 \text{ }\mu\text{m}$ particle suspensions was used. Each antifouling test consisted of

4 cycles, all performed at a pressure of 0.1 MPa . Each cycle could be roughly divided into 3 steps: Step 1, the pure water flux (J_0) was measured when the flow rate became steady and stable; Step 2, pure water was replaced by the $0.2 \text{ }\mu\text{m}$ particle suspension for 30 min; Step 3, the nanofibers membranes were washed with deionized water for 1 h to sufficiently eliminate pollutant, and then the water flux (J_i) was measured again. The flux recovery ratio (FRR) was determined as follows:

$$\text{FRR}(\%) = \frac{J_i}{J_0} \times 100 \quad (4)$$

RESULTS AND DISCUSSION

Morphology of the Electrospun PASS Nanofibers Membranes

Effect of PASS concentration

The structure and diameter of electrospun nanofibers can be significantly influenced by the variation of polymer concentrations.^[24,25] Fig. 2 displays the SEM images of the electrospun PASS nanofibers prepared with various concentrations. When the concentration of spinning solution was 0.20 , 0.21 , or $0.25 \text{ g}\cdot\text{mL}^{-1}$, the nanofibers membrane consisted of beads and fibres. However, the bead number reduced with the increase of polymer solution concentration. When the concentrations were 0.26 and $0.27 \text{ g}\cdot\text{mL}^{-1}$, no beads existed in the whole nanofibers membranes, as seen in Figs. 2(d) and 2(e). In addition, the diameter distribution of nanofibers in the nanofibers membranes was counted. As shown in Figs. 2(d) and 2(e), the nanofibers prepared by $0.27 \text{ g}\cdot\text{mL}^{-1}$ electrospun solution possessed an improved homogeneity and the smaller fiber diameter of $(296 \pm 46) \text{ nm}$. As mentioned in the Introduction part, the membrane with finer fibers may have smaller pore sizes so that $0.27 \text{ g}\cdot\text{mL}^{-1}$ could be regarded as the optimum concentration to obtain the as-prepared PASS nanofibers membrane.

Effect of electrospun voltage

Applied voltage in electrospun process can directly influence the structure of fibers. Fig. 3 shows the effect of applied voltage on the structure of nanofibers at the PASS concentration of $0.27 \text{ g}\cdot\text{mL}^{-1}$ and collector drum speed of $300 \text{ r}\cdot\text{min}^{-1}$. When the applied voltage was 15 kV , Fig. 3(a) indicates that there were some irregular beads formed within the nanofibers membranes. It might be attributed to the fact that the applied voltage was not high enough to keep the electrospun jet in a stable state. As the voltage increased to 20 kV , the beads disappeared completely, and uniform nanofibers were successfully obtained. However, once the voltage further increased to 25 kV , the bead-on-string structure of the nanofibers was observed again. It may be explained by the over-voltage damaging the the stability of the electrospun solution.

Effect of the collecting speed

The speed of collector drum also influences the morphology/structure of electrospun nanofibers because it can adjust the solvent evaporation rate and jet whipping. The effect of collecting speed on the nanofibers micro-structure was investigated with PASS solution concentration of $0.27 \text{ g}\cdot\text{mL}^{-1}$ and the applied voltage of 20 kV . The speed was varied from

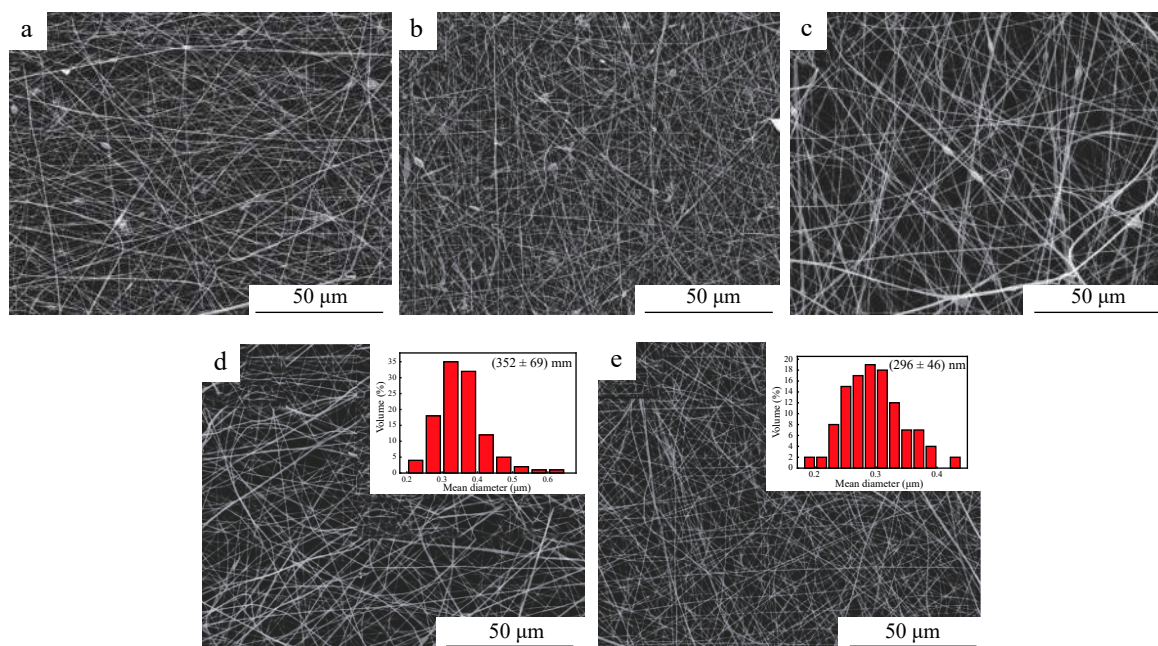


Fig. 2 SEM images of the electrospun PASS nanofibers prepared with different PASS/DMI concentrations: (a) 0.20 g·mL⁻¹, (b) 0.21 g·mL⁻¹, (c) 0.25 g·mL⁻¹, (d) 0.26 g·mL⁻¹, (e) 0.27 g·mL⁻¹ (The applied voltage and the speed of collector drum were 20 kV and 300 r·min⁻¹, respectively.)

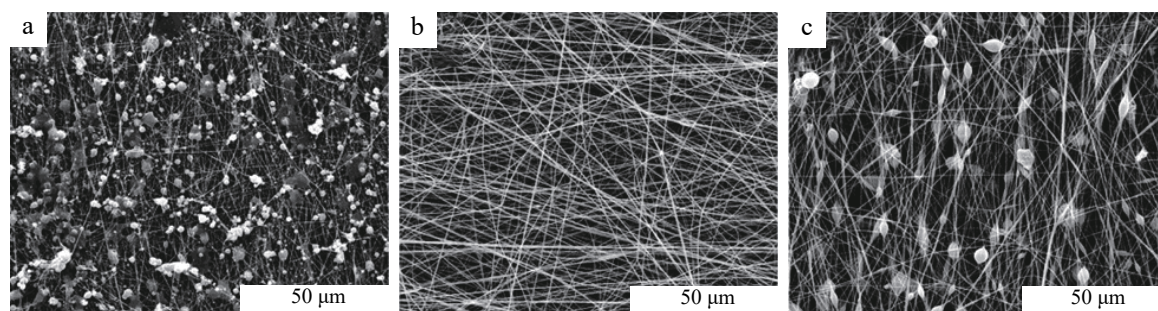


Fig. 3 SEM images of the electrospun PASS nanofibers under different voltages: (a) 15 kV, (b) 20 kV, (c) 25 kV (PASS solution concentration and the speed of collector drum were 0.27 g·mL⁻¹ and 300 r·min⁻¹, respectively.)

100 r·min⁻¹ to 300 r·min⁻¹. Fig. 4 presents the SEM images of nanofibers obtained at the above-mentioned parameters. It can be seen that bead defects were unavoidable at relatively low collecting speed, but when the speed increased to 300 r·min⁻¹, the obtained nanofibers were smooth and had no beads. Meanwhile, incomplete solvent volatilization can also be observed with 100 or 200 r·min⁻¹ of the collecting speed, which could easily damage the fibers structure. The diversification of nanofiber structure may also be caused by the difference of jet stretching.

Based on these studies, following parameters were selected for the fabrication of as-prepared nanofibers membrane: polymer concentration of 0.27 g·mL⁻¹ PASS/DMI, applied voltage of 20 kV, and the speed of collector drum of 300 r·min⁻¹.

Characterization of Multi-layer PASS Membranes

Effect of cold-press pressure on the as-prepared electrospun membrane

To regulate the pore size distribution and mechanical property of the electrospun membranes, a cold-press post-treat-

ment was applied. The membrane morphologies before and after the cold-press treatment under various pressures (at 2.5, 5, 7.5, 10, and 12.5 MPa) were characterized by SEM (Fig. S1, in electronic supplementary information, ESI). A loose structure among the nanofibers can be observed without the pressure, as shown in Fig. S1(a), while an increasingly dense structure can be observed after the cold-press treatment as shown in Figs. S1(b)–S1(f).

It could be also found that the mean surface pore size declined with the increasing cold-press pressure, which has been proved by other studies,^[26,27] but when the higher (10 or 12.5 MPa) cold-press pressure was applied, some nanofibers located in lapping joint could not retain their shapes and became flat. Considering the degree of nanofiber deformation, porosity, and pore size of the electrospun membranes, the cold-press pressure of 10 MPa was chosen to prepare multi-layer PASS nanofibers membranes.

Surface and cross-sectional morphologies of multi-layer PASS membranes

Fig. 5 shows the surface morphologies of the prepared multi-layer PASS nanofibers membranes. As can be seen Fig. 5,

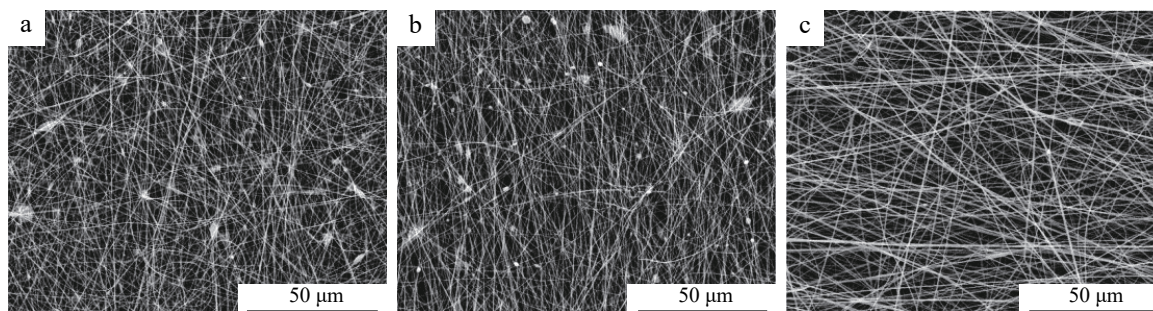


Fig. 4 SEM images of the electrospun PASS nanofibers collected at different speeds: (a) $100 \text{ r} \cdot \text{min}^{-1}$, (b) $200 \text{ r} \cdot \text{min}^{-1}$, and (c) $300 \text{ r} \cdot \text{min}^{-1}$ (PASS solution concentration and the applied voltage were $0.27 \text{ g} \cdot \text{mL}^{-1}$ and 20 kV , respectively.)

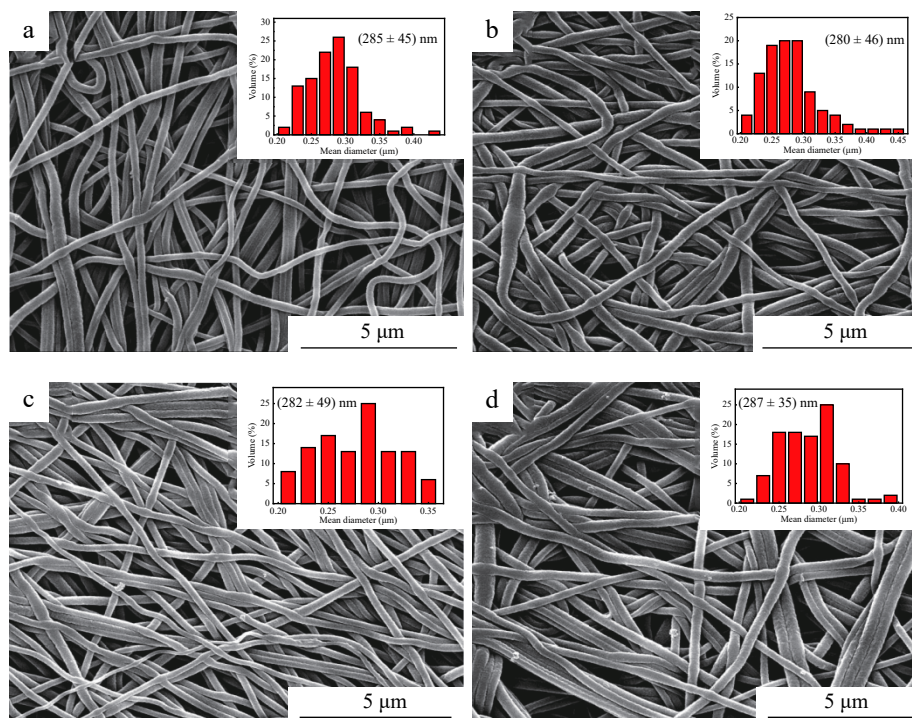


Fig. 5 Surface SEM images of (a) PASS-1, (b) PASS-2, (c) PASS-3, and (d) PASS-6 nanofibers membranes

the mean fibers diameters of PASS-1, PASS-2, PASS-3, and PASS-6 membranes were (285 ± 45) , (280 ± 46) , (282 ± 49) , and $(287 \pm 35) \text{ nm}$, respectively, and only some of the PASS nanofibers at lap joint became flat. These results indicated that the cold-press procedure had little influence on either fiber shapes or diameters. Meanwhile, it was found that the surface pore size and porosity of the PASS MF membranes slightly increased with the thickness augment, as shown in Fig. 5 and Fig. S2 (in ESI). When the cold-press treatment was applied, more nanofibers could be effectively intersected and divided into more small pores, thus a dense structure of nanofibers membranes was obtained. This would contribute to the reduction of pore size and the uniform distribution of nanofibers membrane.

Porosity and pore size of multi-layer PASS membranes

Porosity and pore size were considered as dominant influence factors to the pure water flux and rejection rate of separation membranes.^[19,28] Table 1 lists the porosity, pore size, and thickness of multi-layer PASS nanofibers membranes. The thicknesses of multi-layer PASS membranes in-

creased with the layer increment of as-prepared nanofibers membranes (Table 1). The porosity values of multi-layer PASS nanofibers membranes were substantially decreased from 79.93% to 69.19%, 45.92%, and 38.59%. Meanwhile, the pore sizes of PASS-1, PASS-2, PASS-3, and PASS-6 nanofibers membranes were 1.16–2.85, 1.02–1.99, 0.82–1.64, and 0.29–0.63 μm , respectively. It appeared that the porosity and pore size significantly decreased after the process of cold-pressing different layers of as-prepared nanofibers membrane. Moreover, the pore size distribution became narrower and the dispersion degree of pore diameter decreased with the increasing membranes thickness, which was consistent with SEM observations discussed above. It suggested that the cold-press technique was a facile method for conveniently regulating the pore size of membranes, thereby optimizing the microfiltration performance of the electrospun PASS nanofibers membranes.

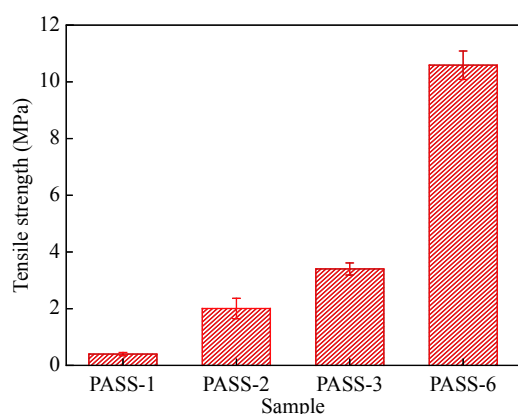
Mechanical properties of multi-layer PASS membranes

The mechanical properties of the surveyed PASS membranes are presented in Fig. 6. Generally, the tensile strength of

Table 1 Porosity, pore size, and thickness of multi-layer PASS nanofibers membranes

Membrane	Porosity (%)	Maximum pore size (μm)	Mean flow pore size (μm)	Minimum pore size (μm)	Thickness (μm)
PASS-1	79.93 ± 0.10	2.85	2.09	1.16	58 ± 5
PASS-2	69.19 ± 1.65	1.99	1.56	1.02	72 ± 4
PASS-3	45.92 ± 1.48	1.64	1.28	0.82	80 ± 7
PASS-6	38.59 ± 1.48	0.63	0.43	0.29	124 ± 5

electrospun fibers membranes was closely related to the geometric arrangement of the fibers and the bonding among fibers.^[29–31] It was clearly shown that the multi-layer PASS nanofibers membranes all exhibited randomly oriented geometry and non-bonding structure. The tensile strengthes of PASS-1, PASS-2, PASS-3, and PASS-6 nanofibers membranes were 0.40, 2.01, 3.40, and 10.59 MPa, respectively. It could be concluded that the cold-press treatment played a positive role in improving mechanical properties of the prepared membranes. This might be due to the increasing packing density and frictional entanglement among PASS nanofibers.

**Fig. 6** Mechanical properties of the multi-layer PASS nanofibers membranes

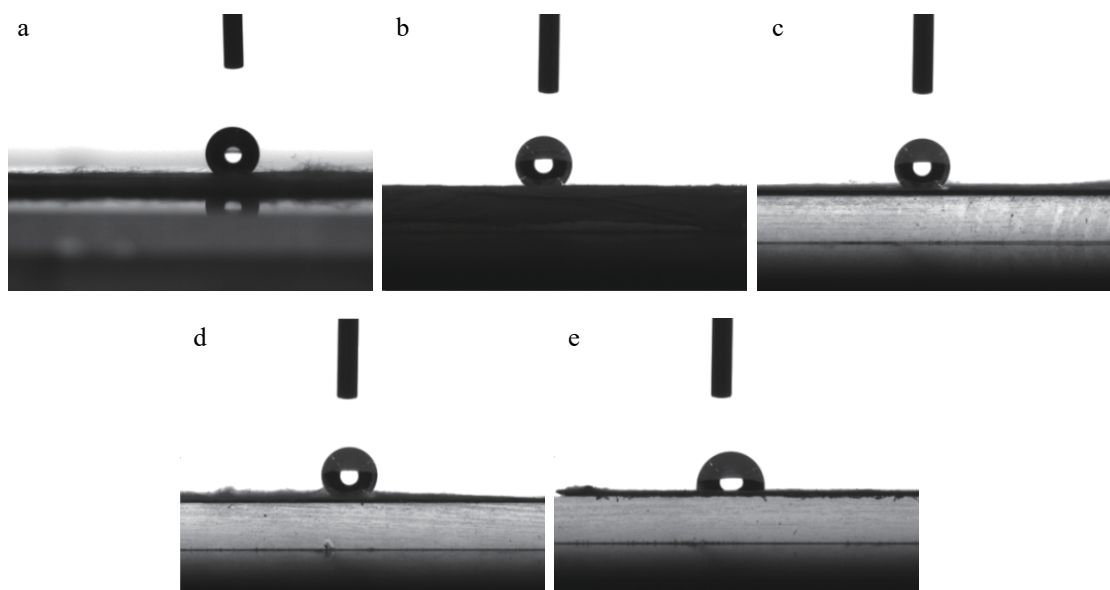
Water contact angles of multi-layer PASS membranes

Pure water flux of separation membranes can be consumingly affected by surface wettability, which is usually measured by the water contact angle. The membrane with lower contact angle generally exhibits higher wettability.^[32] In order to describe the wettability of the prepared electrospun PASS nanofibers membranes, their water contact angles were measured, as shown in Fig. 7. The as-prepared electrospun PASS membrane exhibited hydrophobic behavior with a water contact angle of $(138.2 \pm 1)^\circ$ (Fig. 7a). The contact angles of PASS-1, PASS-2, PASS-3, and PASS-6 membranes were $(137.5 \pm 2)^\circ$, $(135.1 \pm 2)^\circ$, $(132.9 \pm 1)^\circ$, and $(103 \pm 3)^\circ$, respectively. As demonstrated above, the static contact angle of PASS MF membranes decreased when the membrane thickness was increased, which mainly correlated to the surface roughness of the nanofibers membranes.^[33] The decline of water contact angles implied an improved hydrophilicity for membrane surface, which made it favorable for the application in water filtration.

Microfiltration Performance of Multi-layer PASS Membrane

Pure water flux

Pure water flux is one of the key factors to evaluate the microfiltration performance of membranes. The separation membranes with higher flux is expected to possess higher filtration efficiency.^[32] The water flux of multi-layer PASS nanofibers membranes under 0.1 MPa is shown in Fig. 8. It can be observed that the highest pure water flux was attained

**Fig. 7** Water contact angles of (a) as-prepared PASS, (b) PASS-1, (c) PASS-2, (d) PASS-3, and (e) PASS-6 nanofibers membranes

for PASS-1 nanofibers membrane. The water flux values of PASS-1, PASS-2, PASS-3, and PASS-6 membranes were 1041.66, 918.89, 887.27, and 747.76 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, respectively. It is clearly indicated that the pure water flux decreased with the increasing nanofibers membrane thickness, which was mainly due to the decrease of membrane porosity and pore size. The trend of water flux changes was exactly opposite to the nanofibers membrane porosity and pore size, and similar phenomenon was also reported for other filtration membranes.^[29]

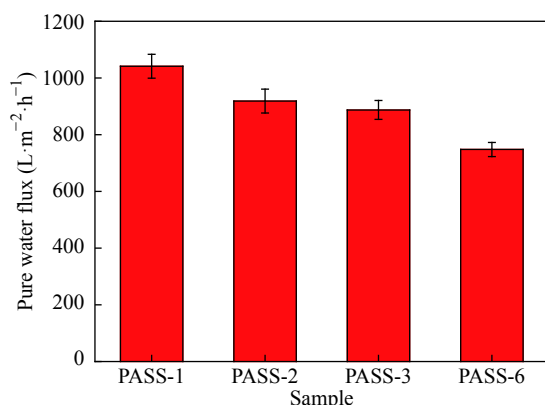


Fig. 8 Pure water flux of multi-layer PASS nanofibers membranes

Rejection rate

The rejection rate to microspheres is another key parameter for MF performance. To evaluate the retention rate of multi-layer PASS nanofibers membranes, 0.5 and 0.2 μm PS particles were chosen as the contaminant models. The rejection rate as a function of membranes thickness is depicted in Fig. 9. It can be found that the filtration efficiency increased as the number of as-prepared PASS nanofibers membrane layers increased. For PASS-3 membrane, the rejection rate was 99.5% and 75.5%, respectively, for 0.5 and 0.2 μm PS particles. However, it should be emphasized that the rejection rate of PASS-6 nanofibers membrane to both particles could reach more than 99.9%. This was consistent with the mean flow pore size of these membranes. The typical photographs of PS solution before and after filtrate are also given in Fig. 9. It is apparent that the slightly blue solution became clear and transparent after filtration process. Therefore, PASS-6 membrane could almost completely remove 0.2 and 0.5 μm particles with high water flux, indicating that cold-pressed electrospun nanofibers membranes exhibited great potential for MF applications.

Antifouling property of the PASS-6 nanofibers membrane

In view of the above results, the PASS-6 nanofibers membrane showed the best microfiltration performance. Thus, the antifouling ability of PASS-6 nanofibers membrane was investigated and the results are shown in Fig. 10. Usually, a higher FRR means a superior antifouling performance.^[32] As seen from Fig. 10, FRR of PASS-6 membrane decreased with the rise of cycle time, but still possessed high flux. FRR of the PASS-6 membrane could be more than 79% of the original pure water flux after four cycles of the recycle treatment.

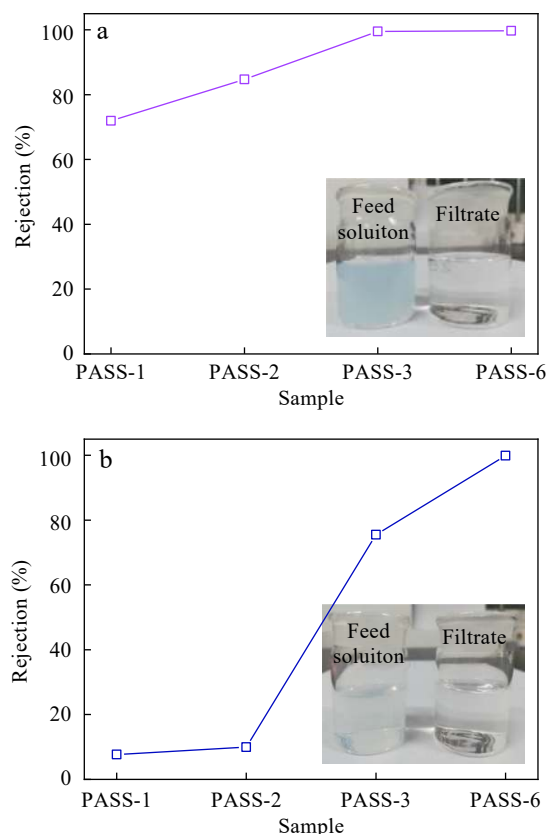


Fig. 9 The rejection rate of multi-layer PASS nanofibers membranes to (a) 0.5 μm and (b) 0.2 μm particles

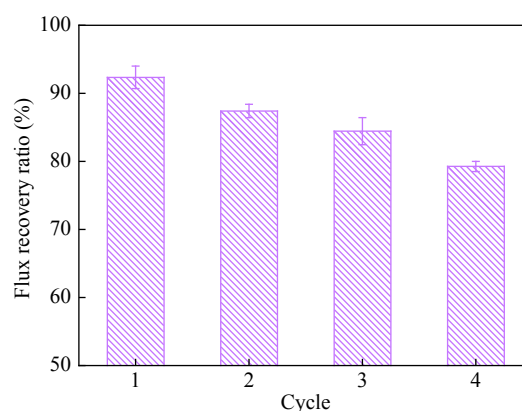


Fig. 10 The flux recovery ratio of PASS-6 nanofibers membrane during four cycles of microfiltration

Considering all the above results, we can conclude that the PASS-6 membranes exhibited good rejection and water flux. The microfiltration properties of the reported electrospun nanofibers membranes are listed in Table 2. The PASS-6 nanofibers membranes exhibited balanced and high-level overall performance in comparison with those of other nanofibers membranes, which illuminate its capability and bright future for water purification as MF membranes.

CONCLUSIONS

In summary, novel nanofibers membranes with excellent microfiltration performance were successfully prepared by

Table 2 Microfiltration performance of various electrospun nanofibers membranes

Membrane	Target contaminant/ particle size	Mean pore size of membranes (μm)	Rejection (%)	Water flux ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$)	Applied pressure (MPa)	Ref.
PVA/PP membranes	Particles/0.5 μm	0.83	96	—	0.02	[19]
PSU membranes	Polystyrene particles/0.5 μm	2.1	47	9000	0.2	[34]
PAN/PET membranes	Polybead carboxylate particles/0.2 μm	0.22	93	4600	0.2	[35]
PS-6/chitosan fibers	Solophenyl red ^a	—	96	—	—	[36]
PHB-CaAlg/CMWCNT membranes	Brilliant blue ^b	—	98.20	32.95	—	[37]
PAN/cellulose nanowhiskers	Polybead particles/0.2 μm	0.22	97.7	1138.7	0.2	[38]
PVDF membranes	Polystyrene particles/0.1 μm	—	98	1300	0.6	[39]
PVDF/GO membranes	Kaolin	0.20	99.9	800	0.1	[40]
PAN nanofibrous membranes	TiO ₂ micro-particles/0.6 μm	0.49	99	~5000	0.5	[41]
PVDF piezoelectric membranes	Kaolin/1.6 μm	0.58	99.87	5573.24	0.1	[42]
PASS-6 membranes	Polystyrene particles/0.2 μm	0.43	99.9	732.88	0.1	This study

^a Solophenyl red: $M_w = 1348.87 \text{ g}\cdot\text{mol}^{-1}$; ^b Brilliant blue: $M_w = 516.54 \text{ g}\cdot\text{mol}^{-1}$

the combination of electrospun PASS nanofibers and cold-press post-treatment. The effectiveness of PASS nanofibers membranes was systematically investigated, and smooth PASS nanofibers with fine diameters of $(296 \pm 46) \text{ nm}$ were obtained under the spinning parameters of $0.27 \text{ g}\cdot\text{mL}^{-1}$ PASS/DMI for the polymer concentration, 20 kV for the applied voltage, and $300 \text{ r}\cdot\text{min}^{-1}$ for the speed of collector drum. Then the multi-layer PASS nanofibers membranes were fabricated by the cold-press method and there were almost no changes in the morphology and diameter except some lapping joints. The porosity and mean pore size of multi-layer PASS membranes decreased when the number of layers increased from 1 to 6. Meanwhile, the thickness and tensile strength of multi-layer PASS membranes increased. It was demonstrated that the cold-press process could effectively regulate the pore size distribution and mechanical properties of nanofibers membranes. Furthermore, the cold-press treatment also had an improving effect on surface wettability of PASS nanofibers membranes. The multi-layer PASS membranes showed gradually rising rejection ratio while the pure water flux decreased with increasing membranes thickness. The water flux of PASS-6 nanofibers membrane was up to $747.76 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, and the membrane could completely reject the 0.2 and 0.5 μm particles from water. The PASS-6 nanofibers membrane also had superior antifouling performance, which made it a promising candidate to remove fine particles or bacteria from wastewater as a microfilter.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2280-6>.

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