High-flux corrugated PDMS composite membrane fabricated by using nanofiber substrate

Jiahui Li, Yang Pan, Wenqi Ji, Haipeng Zhu *, Gongping Liu **, Guangru Zhang, Wanqin Jin

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, 30 Puzhu Road (S), Nanjing, 211816, China

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ABSTRACT
Polydimethylsiloxane (PDMS) is a benchmarked membrane material for pervaporation, gas separation, and nanofiltration, remaining challenges in achieving high-flux membrane. Herein, we proposed a high-flux PDMS membrane with corrugated morphology realized by simply coating PDMS solution on nanofiber substrate. It was demonstrated that the electrospun nanofiber substrate with highly interconnected and porous structures could generate a corrugated PDMS membrane layer with highly increased surface area and meanwhile remarkably reduce transport resistance of the membrane. By optimizing the pore structure of nanofiber substrate and reducing the membrane thickness to sub-micrometer, the corrugated PDMS membrane exhibited up to one order of magnitude higher permeation flux compared with state-of-the-arts PDMS membranes for pervaporation separation of ethanol/water mixtures. Specifically, using a 5 wt% ethanol/water mixture as feed at 60 °C, a total flux of 8.7 kg m⁻² h⁻¹ and a separation factor of 7.2 were obtained. This work provides a facile approach to develop nanostructured membranes with highly enhanced transport properties.

1. Introduction
Polydimethylsiloxane (PDMS) is a benchmarked hydrophobic and rubbery membrane material that has wide applications in pervaporation [1–6], gas separation [7–9] and nanofiltration process [10]. For practical application, a high flux PDMS membrane is always required to enhance the productivity of separation process [8,11]. The membrane flux is primarily determined by the PDMS separation layer. On the one hand, most efforts have been paid to enhance the intrinsic transport properties of membrane material, mainly focusing on incorporating high-performing fillers such as zeolite [12,13] and metal-organic frameworks [3,14,15] into PDMS. The resulting PDMS mixed-matrix membranes exhibited highly enhanced permeability and selectivity, while faced the challenge in fabricating high-flux sub-micron-thick membrane due to the limitation of obtaining ultra-fine fillers.

On the other hand, if we are committed to changing the geometric structure of the membrane to improve the flux, there are two means to control the geometric appearance of the membrane so far. The first method is to make the membrane as thin as possible. It is possible to fabricate ultra-thin membrane with thickness of ~100 nm [5], but it tended to generate membrane defects that deteriorate selectivity. In our previous work, to fabricate PDMS/CHNs/PAN composite membranes with a membrane thickness of less than 200 nm, a multiple and alternate spin-coating process was devised in collaboration with the interface-decoration layer of CHNs (copper hydroxide nanofibers) [16]. It achieved excellent butanol/water mixtures separation performance. Furthermore, recent works has shown that the mass transfer resistance of substrate layer has a substantial influence on the entire pervaporation separation ability of PDMS membranes [17–19].

The second method is patterning the composite membrane surface that increasing the surface roughness or membrane-effective area could increase the permeation flux. Cussler et al., fabricated a highly corrugated PDMS membrane for pervaporation experiments and verified the modified Thiele model for membrane mass transfer. It was found that the corrugated membrane structure leads to doubling of flux compared to flat membranes [20]. However, no selective permeation was reported in this kind of PDMS membrane, which could not exclude the influence of defects on the increase of membrane flux. Also, this high-flux PDMS membrane did not effectively separate molecular mixtures. Li et al., prepared PDMS selective layers by using different crosslinking agents...
(p-tolyltriethoxysilane, p-TTES; Triethoxyvinylsilane, VTES; Tetraethyl orthosilicate, TEOS), and found that the membrane crosslinked by TEOS having the biggest pattern size (3.78 μm). They attributed the high flux of patterned membrane compared to the non-patterned membrane to the increase of effective membrane area [21]. Additionally, patterned membranes were also explored for other kinds of membrane materials, including polymers and inorganics. Turing-type polyamide reverse osmosis membranes for water desalination were prepared by controlled interfacial polymerization. It was demonstrated that the Turing structures have a significant effect on the water permeance [22]. Unfortunately, such interfacial polymerization is not suitable for fabricating high-flux rubbery polymeric membranes. Huang et al., reported the growth of MOF crystalline membranes on highly complex patterned substrates. The recessed portion of the patterned surface resulted in a higher permeation flux as well as an increase in the membrane area [23].

Ideally, fabrication of high-flux PDMS membrane lies in depositing thinner membrane layer on a macro-porous support, and creating patterned membrane surface if possible. However, it remains a great challenge to achieve a submicron-thin PDMS membrane as using a conventional macro-porous substrate (e.g., average pore size >100 nm). Because PDMS coating infiltration into the substrate large pores frequently result in a thick transition layer and/or defects in membrane layer that decrease the membrane separation performance. Moreover, the current methods to fabricate patterned PDMS membranes are complicated and/or failed to show promising separation performance for molecular mixtures.

To address the challenges of fabricating high-flux PDMS membrane, on the basis of experiment observations, we demonstrated that a defect-free and submicron-thin PDMS membrane can be easily fabricated by coating PDMS solution on an electrospun nanofiber substrate (Fig. 1). The surface nanofiber interpenetrated structure of the substrate prevented excessive penetrating of the PDMS solvent into large pores of the substrate, and plenty of corrugated structures were formed on the PDMS composite membrane surface in the meantime. The resulting high-flux corrugated PDMS composite membrane has the following features: (1) simple membrane preparation process; (2) no specific substrate mold is required; (3) extremely low transport resistance of nanofiber substrate. Pervaporation of ethanol/water mixtures—a typical separation system for the application of PDMS membrane—was used to explore the pervaporation property of the corrugated PDMS membrane.

2. Experimental

2.1. Materials

Dihydroxypropyldimethylsiloxane (PDMS, Mw = 60,000) was obtained from Shanghai Resin Factory Co., Ltd. Commercial polymer poly(vinylidene fluoride) (PVDF, Mw = 500,000) was produced by Kureha Co., Ltd, Japan. Dibutyltin dilaurate (DBTDL, ≥95%) was supplied by Shanghai Aladdin Co., Ltd. China. Isopropanol alcohol (IPA), ethanol, N,N-Dimethylformamide (DMF), tetraethyl orthosilicate (TEOS), and n-heptane were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Acetone was supplied by Shanghai Lingfeng Chemical Reagent Co., Ltd, China. The wetting fluid (low surface tension) was supplied by Shuyihui Scientific Instrument Co., Ltd, Nanjing, China. In all of the experiments, deionized water was used. Commercial PVDF flat-sheet substrate (average pore size: 0.25 μm) was utilized to compare with the PDVF nanofiber membranes in this study.

2.2. Membrane fabrication

The preparation procedures to fabricate nanofiber substrates are as follows. PVDF was dissolved in DMF and acetone mixed solution (4:1) by stirring in the oil bath (~60 °C) for 24 h to get spinning solution containing 10 wt% PVDF. The PVDF spinning solution was installed in a 10 mL injection with a 0.5 mm inner diameter blunt metal needle and was electrospun onto a poly (ethylene terephthalate) (PET) nonwoven substrate. The syringe speed was maintained at 0.2 mL/min. The speed of the rotating collector wrapped in PET nonwoven substrate was 300 rpm. The voltage was set at 15 kV, and the collector was 20 cm away from the metallic needle. The electrospun processes were carried out with relative humidity of 40–50% at room temperature. The electrospun nanofiber substrates were hot-pressed to improve the structural integrity and mechanical strength. They were given the name X-Y-PVDF, with X denoting the temperature and Y denoting the pressure of the hot-pressing post-treatment.

The preparation of PDMS solution was followed by our earlier research [24]. In a nutshell, catalyst DBTDL and crosslinker TEOS were added to the mix solution after PDMS was dissolved in n-heptane. The DBTDL, TEOS, and PDMS were mixed combined in a 1:10:100 mass ratio and agitated at room temperature for 24 h. To generate an active layer, a specified amount of PDMS solutions were spun-coated (250 rpm, 9 s; 3000 rpm, 40 s) on PVDF nanofiber substrates. The membrane was then heated in a 25 °C vacuum oven for another 12 h after being exposed to air for 12 h.

2.3. Characterizations

The structure and morphology of nanofiber membranes were analyzed using a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan). With atomic force microscopy, the three-dimensional topography of the membrane surface was determined (AFM, Bruker Dimension Icon, American, tapping mode). The software program NanoScope Analysis 1.9 was used to process the AFM images. The energy dispersive X-ray spectrometer (EDX) was used to evaluate the element mapping. A contact angle Drop-Meter (A-100, HaiShu Maishi Co., Ltd, Ningbo, China) was measured the water contact angles on the membrane surface. The pore size distribution of PVDF substrates was measured by the SYH-60 membrane performance analyzer (Shuhihui Scientific Instrument Co., Ltd, Nanjing, China).
2.4. Test of substrates’ pure ethanol permeance, pore size, and porosity

A SYH-60 equipment with liquid ejection method was measured the pore size distribution of membranes [25]. A cross-flow filtration system was utilized to assess the ethanol permeance at 25 °C and 0.1 bar to determine the substrate transport resistance. The permeance of pure ethanol was determined as follows:

\[ P = \frac{V}{A \Delta p \cdot t} \]  (1)

where \( P \) is the permeance of pure ethanol, \( L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1} \); \( V \) is the volume of permeate ethanol, \( L \); \( \Delta p \) is the pressure differential across the transmembrane, bar. \( A \) is the effective membrane area, \( m^2 \). \( t \) is the effective time, h.

The porosity of the substrate was determined by dividing the pore volume by the total volume of the substrate. The wetting fluid was isopropyl alcohol (IPA). The substrate was put in IPA for 12 h, and was weighted before and after saturation. The substrate porosity (\( \varepsilon \)) was calculated as follows:

\[ \varepsilon = \frac{(w_w - w_d) / \rho_i}{w_w / \rho_i + w_d / \rho_p} \]  (2)

where \( w_d \) is the weight of the dry substrate, g; \( w_w \) is the weight of the wet substrate, g; \( \rho_i \) is the isopropyl alcohol density, g/cm\(^3\); \( \rho_p \) is the polymer density, g/cm\(^3\).

2.5. Pervaporation test of ethanol/water mixtures

The pervaporation experiment was done with a handmade equipment, and the penetrated vapor was captured with a liquid nitrogen cold trap. The membrane was fitted in the stainless-steel membrane module with an effective membrane area of 2.27 cm\(^2\). The oil bath kept the feed temperature between 30 and 60 °C. The pressure downstream was...
maintained below 250 Pa using a vacuum pump. To ensure that the permeation data were accurate, at least three samples were obtained for each membrane. The pervaporation performance was typically measured in terms of separation factor and total flux. A gas chromatograph was used to measure membrane feed and permeate concentration (Shimadzu, GC-2014, Japan).

The total flux ($J$, kg m$^{-2}$ h$^{-1}$) and separation factor ($\beta$) were determined as follows:

$$ J = \frac{Q}{A \cdot t} \quad (3) $$

$$ \beta = \frac{y_e / y_w}{x_e / x_w} \quad (4) $$

where $Q$ is the total weight of permeate collected in operating time, kg; $t$ is the permeation time interval for the pervaporation, h; $A$ is the effective membrane area, m$^2$. Besides, $x$ and $y$ are the mass fractions of water (w) or ethanol (e) in the feed and permeate sides.

Table 1
Characteristics of PVDF nanofiber substrates prepared with various conditions.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Hot-pressing pressure (MPa)</th>
<th>Hot-pressing temperature (°C)</th>
<th>Water contact angle (°)</th>
<th>Average pore size (nm)</th>
<th>Porosity (%)</th>
<th>Ethanol permeance (L m$^{-2}$ h$^{-1}$ bar$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>1</td>
<td>80</td>
<td>128.8</td>
<td>307</td>
<td>76.5 ± 1.6</td>
<td>13455.7</td>
</tr>
<tr>
<td>S2</td>
<td>3</td>
<td>80</td>
<td>127.7</td>
<td>279</td>
<td>65.7 ± 1.2</td>
<td>7413.3</td>
</tr>
<tr>
<td>S3</td>
<td>5</td>
<td>80</td>
<td>122.2</td>
<td>259</td>
<td>58.4 ± 1.1</td>
<td>6794.6</td>
</tr>
<tr>
<td>S4</td>
<td>7</td>
<td>80</td>
<td>121.4</td>
<td>180</td>
<td>53.8 ± 1.5</td>
<td>4991.2</td>
</tr>
<tr>
<td>S5</td>
<td>9</td>
<td>80</td>
<td>120.6</td>
<td>165</td>
<td>46.6 ± 2.1</td>
<td>2752.9</td>
</tr>
<tr>
<td>S6</td>
<td>7</td>
<td>55</td>
<td>132.9</td>
<td>260</td>
<td>76.4 ± 1.7</td>
<td>15074.7</td>
</tr>
<tr>
<td>S7</td>
<td>7</td>
<td>40</td>
<td>126.6</td>
<td>227</td>
<td>63.9 ± 1.6</td>
<td>11028.8</td>
</tr>
<tr>
<td>S8</td>
<td>7</td>
<td>55</td>
<td>132.9</td>
<td>211</td>
<td>62.1 ± 1.9</td>
<td>7302.0</td>
</tr>
<tr>
<td>S9</td>
<td>7</td>
<td>70</td>
<td>129.1</td>
<td>194</td>
<td>54.0 ± 2.5</td>
<td>6960.8</td>
</tr>
<tr>
<td>C1</td>
<td>–</td>
<td>–</td>
<td>121.0</td>
<td>250</td>
<td>54.9 ± 3.5</td>
<td>3050.3</td>
</tr>
</tbody>
</table>

Fig. 3. Influence of pressure and temperature of hot-pressing on the pure ethanol permeance, porosity, and average pore size of the PVDF nanofiber substrates.

Fig. 4. SEM surface (a, d), cross-sectional views (b, e) and Si element EDX mapping (c, f) images of (a–c) defect-free PDMS membrane layer formed on PVDF nanofiber substrate with suitable pore size (S3, 259 nm); (d–f) defective PDMS membrane layer formed on PVDF nanofiber substrate with oversize pores (S1, 307 nm).
3. Results and discussion

3.1. Effect of substrate pore sizes

PVDF nanofiber substrate is fabricated by electrospinning technique [26]. The SEM images in Fig. 2A-C demonstrate that the surface morphology and digital image (6.5 cm × 6.5 cm) of as-spun PVDF nanofiber substrate. The electrospun PVDF nanofiber substrate has a porous structure with strongly interpenetrated fibers, and there is no thick skin layer, as can be seen. Such nanostructures of nanofiber substrate are favorable for forming corrugated polymer coating and low transport resistance.

To tune the pore structure and improve the mechanical strength, the electrospun PVDF nanofiber substrates were post-treated by hot-pressing at various pressures and temperatures. Surface morphology and pore size distribution, and porosity, average pore size and ethanol permeance are displayed in Figs. 2 and 3, respectively. All the details of the substrates are given in Table 1. It can be observed that the increase in hot-pressing pressure and/or temperature generated a more compact and rigid structure of the PVDF substrate. This achieved a reduction in pore size and porosity, which would lead to an increase of transport resistance. Alternatively, if the substrate pore size and porosity are oversized, it is harder to produce a defect-free membrane on the substrate surface [27].

Moreover, after different pressures and temperatures of hot-pressing post-treatment, water contact angle of PVDF nanofiber substrates is essentially unchanged. The substrate surface show strong hydrophobicity, displaying water contact angles higher than 120°. Such low surface energy of the substrate lead to the easily wetting of non-polar liquid (e.g., PDMS/heptane coating solution) that benefits for forming a defect-free membrane layer. As a result, PDMS casting solution can be directly coated on the substrate surface, forming a defect-free and thin PDMS membrane layer.

Subsequently, we investigated the fabrication of PDMS membrane on PVDF nanofiber substrates with different pore sizes. As shown in Fig. 4a–c, a defect-free PDMS layer (membrane thickness: ~500 nm) is formed on the PVDF nanofiber substrate with substrate pore size of 259 nm (S3). From the surface morphologies of the PDMS/PVDF composite membrane, it is extremely rough, showing a corrugated structure. In this work, it is distinguished as corrugated PDMS membrane. When separating a 5 wt% ethanol/water mixture at a feed temperature 40 °C, the total flux of these corrugated PDMS membranes was 1.9–3.9 kg m⁻² h⁻¹, with a separation factor of more than 7 (Fig. 5).

However, further increasing the substrate pore size to more than ~300 nm, defects emerged in the PDMS membrane layer (Fig. 4d–e), leading to a substantial fall in the ethanol-water solution separation factor to 5.83 (Fig. 5). This value is below the intrinsic selectivity of PDMS membrane material [5]. As evidenced by the EDX mapping of Si element (from PDMS) along the cross-sectional view of PDMS/PVDF nanofiber composite membrane (Fig. 4c, f), the PDMS coating intrusion into the substrate with pore size of ~307 nm is much significant than the PDMS coated on the substrate with pore size of ~259 nm.

3.2. Optimization of the thickness of PDMS layer

With the PVDF nanofiber substrate having a suitable pore size, we aimed to gradually reduce the thickness of the PDMS membrane layer until it is defect-free in order to further increase the flux of the PDMS/PVDF composite membrane. In general, decreasing the PDMS thickness
Fig. 7. AFM images of smooth PDMS membrane (a), and corrugated PDMS membranes (b–c); membrane thickness: (a) 2.5 μm; (b) 1.5 μm; (c) 0.5 μm.

Fig. 8. Pervaporation properties of PDMS/PVDF nanofiber composite membranes at different membrane thicknesses (feed conditions: 5 wt% ethanol/water, 40 °C).

Fig. 9. SEM images of (a–c) surface and (d–f) cross-sectional views of conventional PVDF substrate (a, d) and its PDMS/PVDF composite membranes with ~0.5 μm (b, e) or ~2.5 μm (c, f) membrane thickness.
can improve the total flux of the membrane without defective pores [28-30]. As shown in Fig. 6, defect-free PDMS membrane layers of varied thicknesses of 2.5 μm, 1.5 μm, and 0.5 μm were successfully prepared on the PVDF nanofiber substrate (S3). At least three membrane samples were observed by SEM and an average value of the PDMS layer thickness is reported here. As the membrane thickness is less than 0.5 μm, it is more likely to form defects. Also, the reproducibility of membrane fabrication was lower, and mechanical stability decreased.

It is interesting to notice the surface morphology evaluation in the PDMS/PVDF nanofiber composite membranes with varying membrane thicknesses. According to Fig. 6a–c, the corrugated morphology of PDMS membrane layer gradually revealed as its thickness decreases. We further employed AFM to monitor the surface morphology of these PDMS composite membranes (Fig. 7). It is confirmed that the nanofiber interpenetrated structures of PVDF substrate produced a corrugated membrane surface. Moreover, the corrugated morphology was indicated by the 2-3-fold increase of height as decreasing the thickness of PDMS membrane layer. Importantly, such corrugated morphology effectively increases the membrane surface area, which was determined by using NanoScope Analysis software of AFM [22]. As given in Fig. 8a, the increase percentage in surface area of the corrugated PDMS membrane with thickness of ~500 nm was 25.7%, which is one order of magnitude larger than that of smooth PDMS membrane (2.5%). The permeation flux of PDMS/PVDF nanofiber composite membrane would be greatly enhanced due to the dramatically increased surface area.

The influence of smooth and corrugated membrane surfaces on PDMS/PVDF nanofiber composite membrane separation performance was thus examined. Fig. 8b demonstrates that the total flux was enhanced from 1.9 to 3.9 kg m⁻² h⁻¹ by reducing the membrane thickness from 2.5 to 0.5 μm, whereas the ethanol-water solution separation factor was well retained. The higher flux in the thinner PDMS composite membrane can be attributed to two aspects: i) lower transport resistance in thinner membrane layer; ii) higher surface area provided by the corrugated morphology. It was discovered that the membrane flux does not linearly increase as the membrane thickness decreases (membrane thickness <0.5 μm), reflecting the contribution of the transition layer to the overall transport resistance across the composite membrane. Generally, a thicker transition layer was formed as fabricating thinner PDMS membrane, as coating less viscous PDMS solution onto the substrate would cause more instruction of the solution into the substrate pores [31].

3.3. Comparison with PDMS membranes fabricated by conventional substrate

To further understand the effect of nanofiber substrate on the formation and pervaporation property of PDMS composite membrane, we compared it with conventional substrate for PDMS membrane. As shown in Fig. 9a and d, conventional PVDF substrate derived from non-solvent or thermal induced phase separation has a leaf crystal-like irregular pores [32]. Because of the distinct pore structures, the pure ethanol permeance of conventional PVDF substrate (C1) was only half of that of the PVDF nanofiber substrate (S3) with similar pore size and porosity (Table 1). By using the same PDMS polymer solution, we prepared defect-free PDMS membrane layer (membrane thickness: 0.5–2.5 μm) on the conventional PDVF substrate. Fig. 9b–c and e–f depicts surface and cross-sectional views SEM images. Compared with nanofiber substrate, the major difference of using conventional substrate is the much smoother membrane surface when fabricating a sub-micron thick PDMS membrane layer (Fig. 9b vs Fig. 6c).

Furthermore, the PDMS/PVDF composite membranes (membrane thickness: 0.5 μm or 2.5 μm) separation performance with nanofiber or conventional substrate was compared in Fig. 10. With the membrane thickness of 0.5 μm, the conventional substrate resulted in a less selective PDMS membrane layer with 2.2 times lower permeation flux compared with the nanofiber substrate. As the membrane thickness increases to 2.5 μm, the separation factor of PDMS membrane fabricated by both substrates are very close, while the total flux of the conventional substrate fabricated membrane is 1.8 times lower than the nanofiber substrate fabricated membrane. To explain the significant enhancement of flux in the PDMS/PVDF nanofiber composite membranes, the major factor can be attributed to the lowering of mass transfer resistance of the composite membrane, as evidenced by the much higher pure ethanol permeance of the nanofiber substrate than that of conventional substrate. The secondary factor could be the increase of surface area in the......
PDMS membrane layer owing to the corrugated morphology. Indeed, it is found that the multiple of flux increase in the thinner PDMS membrane (0.5 μm) with more obvious corrugated surface (2.2 times) is larger compared with thicker PDMS membrane (2.5 μm) with much smoother surface (1.8 times). Additionally, compared with conventional PVDF substrate, the pore penetration of polymer solution into the nanofiber substrate could be reduced and more dilute polymer solution could still form thin and defect-free membrane layer on the highly interconnected porous nanofiber structures. The reduce pore penetration can also explain the slight higher separation factor in the PDMS/PVDF composite membrane with nanofiber substrate than that with conventional substrate.

3.4. Effect of operation conditions on the separation performance

We further investigated the membrane separation performance under several important operation circumstances, such as feed concentration, operating temperature, and operation time, to determine the application feasibility of the corrugated PDMS/PVDF nanofiber composite membrane. As depicted in Fig. 11a–b, the total flux increases from 3.2 to 4.8 kg m⁻² h⁻¹ as the ethanol percentage in the feed varies from 2.5 to 10 wt%, while the separation factor drops from 7.8 to 6.4. The increased flux is due to the enhanced driving force resulting from the more ethanol adsorption in the membrane as the ethanol concentration rises. The decreased separation factor is due to membrane swelling caused by high ethanol concentrations, which allows water molecules to easily permeating through the membrane more easily. The slightly lower water flux at higher ethanol content implies that the water permeation might be hindered by the large amount of ethanol molecules adsorbed in the PDMS membrane.

Though the total flux rises dramatically as the operating temperature rises, the separation factor decreases marginally, as depicted in Fig. 12a. The increase of temperature affects the molecular transport through the PDMS membrane in two aspects. First, it increases the driving force of pervaporation process. Second, it would enlarge the free volume of PDMS membrane [33]. Since water has a lower molecular kinetic diameter than ethanol, the water flux increases faster than ethanol flux when the temperature is increased, which leads to a slight decrease in separation factor. According to the Arrhenius equation [34] (Fig. 12b), the activation energies of pervaporation (E_p) for water and ethanol permeation were determined, respectively. The activation energies of ethanol and water via corrugated PDMS membranes are 31.5 kJ/mol and 34.1 kJ/mol, respectively, according to the equation. This indicates that water is more temperature sensitive than ethanol. As the operating temperature is 60 °C, the total flux reaches up to 8.7 kg m⁻² h⁻¹ and the separation factor is as good as 7.2. Overall, the corrugated PDMS/PVDF nanofiber composite membrane performed well in separating ethanol-water solutions under a variety of operating conditions.

Fig. 12. Pervaporation permeance of corrugated PDMS/PVDF nanofiber composite membrane at different operating temperatures (a-b, feed concentration: 5 wt% ethanol/water): (a) total flux and separation factor; (b) Arrhenius plots in separating 5 wt% ethanol/water separation.

Fig. 13. Extended trial of corrugated PDMS/PVDF nanofiber composite membrane in separating 5 wt% ethanol/water at 40 °C.

Fig. 14. Pervaporation performance comparison of state-of-the-arts PDMS membranes in separating ethanol-water solution (more details are given in Table 2).
Table 2

Pervaporation properties comparison of PDMS membranes of ethanol-water mixtures.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Ethanol in feed (wt%)</th>
<th>Temperature (°C)</th>
<th>Membrane thickness (µm)</th>
<th>Flux (kg m⁻² h⁻¹)</th>
<th>Separation factor</th>
<th>Reference</th>
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<tr>
<td>PDMS-vinyl</td>
<td>10</td>
<td>40</td>
<td>82</td>
<td>0.1</td>
<td>8.6</td>
<td>[35]</td>
</tr>
<tr>
<td>Patterned PDMS</td>
<td>6</td>
<td>37</td>
<td>10</td>
<td>0.8</td>
<td>8.4</td>
<td>[21]</td>
</tr>
<tr>
<td>PDMS</td>
<td>5</td>
<td>60</td>
<td>–</td>
<td>1.2</td>
<td>8.2</td>
<td>[36]</td>
</tr>
<tr>
<td>PDMS/ceramic</td>
<td>5</td>
<td>40</td>
<td>–8</td>
<td>1.2</td>
<td>8.1</td>
<td>[37]</td>
</tr>
<tr>
<td>PDMS/PVDF</td>
<td>5</td>
<td>40</td>
<td>10</td>
<td>0.5</td>
<td>8.3</td>
<td>[38]</td>
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<td>PDMS/PTEK</td>
<td>5</td>
<td>40</td>
<td>0.7</td>
<td>2.4</td>
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<td>[39]</td>
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<td>PDMS/CA</td>
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<td>8</td>
<td>1.3</td>
<td>8.5</td>
<td>[40]</td>
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<td>PDMS/PS</td>
<td>5</td>
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<td>–1</td>
<td>3.3</td>
<td>7.5</td>
<td>[41]</td>
</tr>
<tr>
<td>PDMS/PDMS</td>
<td>5</td>
<td>60</td>
<td>–</td>
<td>1.5</td>
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<td>[42]</td>
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<td>Corrugated PDMS</td>
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<td>3.9</td>
<td>7.6</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>5</td>
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<td>7.6</td>
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<tr>
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<td>60</td>
<td>0.5</td>
<td>8.7</td>
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</tbody>
</table>

Long-term stability is another key factor to evaluate the membrane performance toward commercial application. During 500 h of continuous pervaporation separation of a 5 wt% ethanol-water solution at 40 °C, the corrugated PDMS/PVDF nanofiber composite membrane displayed stable performance, as illustrated in Fig. 13. The average total flux is 4.1 kg m⁻² h⁻¹ and separation factor is 7.3. The proper application of PDMS coating to the highly interconnected and porous nanofiber substrate results in a favorable interface between substrate and polymer layer, thereby enhancing the bond between membrane layer and substrate. As a conclusion, the sub-micrometer thick PDMS composite membrane can achieve desirable long-term operation stability.

3.5. Comparison of separation performance with literatures

Over the past three decades, there have been a lot of reports on PDMS membranes for organophilic pervaporation separation. In this work, Fig. 14 and Table 2 highlight the separation performance of newly reported PDMS membranes for pervaporation of ethanol-water solution. Owing to its nanofiber substrate pore structure and corrugated morphology of membrane surface, the corrugated PDMS membrane shows outstanding separation performance, which is expected to be a promising high-flux membrane for ethanol-water mixture separation. Together with the robust structural stability, the highly enhanced permeation flux with well-preserved separation factor at higher operating temperature or feed ethanol concentration are favorable for the practical application. Toward industrial application, the scale-up fabrication of nanofiber substrate and the subsequent PDMS coating should be further studied, and the long-term stability under realistic feed conditions of the PDMS/PVDF nanofiber composite membrane requires systematic investigations.

4. Conclusions

In conclusion, we fabricated a new type of corrugated PDMS membrane by directly coating polymer solution on an electrospun nanofiber substrate. The corrugated morphology of the membrane surface, and the highly inter-connected and porous nanofiber substrate were propitious to the remarkable enhancement in membrane flux, leading to the outstanding separation performance compared with state-of-the-arts PDMS membranes. The sub-micron thick corrugated PDMS membrane displayed a total flux of 8.7 kg m⁻² h⁻¹ and a separation factor of 7.2 for separating 5 wt% ethanol/water mixtures at 60 °C. This facile fabrication approach based on nanofiber substrate coating shows great potential in development of corrugated polymeric membranes and high-flux membranes.

CRediT authorship contribution statement


Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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