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A novel electrospun, hydrophobic, and elastomeric styrene-butadiene-styrene membrane for membrane distillation applications

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1 **Abstract:** In this study, a novel hydrophobic, microporous membrane was fabricated from
2 styrene-butadiene-styrene (SBS) polymer using electrospinning and evaluated for membrane
3 distillation applications. Compared to a commercially available polytetrafluoroethylene (PTFE)
4 membrane, the SBS membrane had larger membrane pore size and fiber diameter and
5 comparable membrane porosity. The fabricated SBS showed slightly lower water flux than the
6 PTFE membrane because it was two times thicker. However, the SBS membrane had better salt
7 rejection and most importantly could be fabricated via a simple process. The SBS membrane was
8 also more hydrophobic than the reference PTFE membrane. In particular, as temperature of the
9 reference water liquid increased to 60 °C, the SBS membrane remained hydrophobic with a
10 contact angle of 100° whereas the PTFE became hydrophilic with a contact angle of less than
11 90°. [The hydrophobic membrane surface](#) prevented the intrusion of liquid into the membrane
12 pores, thus improving the salt rejection of the SBS membrane. In addition, the SBS membrane
13 had superior mechanical strength over the PTFE membrane. Using the SBS membrane, stable
14 water flux was achieved throughout an extended MD operation period of 120 hours to produce
15 excellent quality distillate (over 99.7% salt rejection) from seawater.

16 **Keywords:** *membrane distillation (MD); styrene-butadiene-styrene (SBS); membrane*
17 *fabrication; electrospinning; seawater desalination.*

18 **1. Introduction**

19 Seawater desalination is an effective approach to address fresh water scarcities in many
20 coastal cities around the world [1]. Recent technological progress in membrane technology has
21 allowed for cost-effective seawater desalination even for municipal potable water supply. Indeed,
22 there has been a significant increase in membrane based (especially reverse osmosis (RO))
23 seawater desalination plants in recent years [2]. In 2016, an estimated US \$21 billion was
24 invested on RO seawater desalination plants and this figure is expected to be doubled by 2020
25 [2]. However, the carbon footprint of seawater desalination is still high. Thus, there have also
26 been many dedicated attempts to develop new membrane desalination technologies such as
27 membrane distillation (MD) that can be readily coupled with renewable solar and geothermal
28 energy [3].

29 MD is an emerging process with significant potential for seawater desalination applications
30 [4-10]. The MD process combines thermal distillation and membrane separation. In MD, the hot
31 saline water feed is in contact with a hydrophobic and microporous membrane. The hydrophobic
32 nature of the membrane prevents liquid water from penetrating into the membrane pores while
33 allowing for the permeation of water vapour. The difference in temperature across the membrane
34 induces a water vapour pressure gradient from the feed to the distillate side, thus allowing for
35 water vapour transport through the membrane pores. Since only water vapour can be transported
36 across the membrane, in theory MD can offer complete salt rejection [11, 12]. In addition, unlike
37 pressure-driven membrane processes (i.e. RO), MD operation does not require a high hydrostatic
38 pressure. As a result, inexpensive non-corrosive materials such as plastics can be used for MD
39 system construction. Finally, because heat is the primary energy input into the MD process, the
40 energy costs of seawater MD desalination can be greatly reduced when low-grade heat sources
41 such as waste heat or thermal energy can be tapped on [13-15]. Given these attributes, MD has
42 emerged as an ideal technology platform for small-scale, off-grid, and low-cost seawater
43 desalination processes [16-18].

44 Commercial realisation of seawater MD desalination has been constrained in part by the lack
45 of suitable membrane materials [7, 19]. Given the many essential attributes of the MD membrane
46 such as high hydrophobicity, uniform porosity, and low thermal conductivity, to date, only a few
47 hydrophobic polymers have been used to fabricate MD membranes [20, 21]. The fabrication of
48 most current MD membranes is a complex process involving many toxic chemicals (e.g. solvents
49 and volatile lubricating agents) [7, 19]. In addition, current MD membrane materials such as
50 polytetrafluoroethylene (PTFE) and polyvinylidene difluoride (PVDF) are not biodegradable.
51 Thus, their disposal at the end of the membrane lifetime is a significant environmental issue.

52 There is a growing interest in new MD membrane materials to overcome the above-
53 mentioned limitations. One of such novel materials is styrene-butadiene-styrene (SBS). SBS is a
54 hydrophobic, thermoplastic elastomer with low thermal conductivity (i.e. 180 mW/m.K
55 compared to 259 mW/m.K of PTFE) and excellent mechanical strength for membrane
56 applications [22-24]. The cost of SBS is significantly lower than that of PVDF and particularly
57 PTFE that are currently used for MD membrane fabrication. In addition, SBS is readily
58 degradable and thus the disposal issue at the end of the membrane lifetime can be negated.
59 Indeed, pervaporation membranes have been successfully fabricated from SBS via a simple
60 solvent evaporation technique [22]. Several previous studies have demonstrated successful
61 applications of these pervaporation SBS membranes for ethanol enrichment [22] and the removal
62 of volatile organic compounds from wastewater [25]. In this work, we report an electrospinning
63 approach to fabricate SBS membrane for MD applications. Unlike conventional membrane
64 fabrication methods such as sintering and melt-extrusion methods, electrospinning involves only
65 a few simple processes that can be effectively tailored to obtain membranes with desirable
66 features for MD applications [26-28]. Electrospinning is also a versatile technique that is
67 compatible with a range of polymeric materials and solvents [26].

68 The fabricated electrospun SBS membrane and a commercial MD membrane made from
69 PTFE were evaluated and compared. Firstly, the key properties (e.g. surface morphology,
70 wettability, and mechanical strength) of the fabricated SBS and commercial PTFE membranes
71 were characterised and compared. Then, water flux and mass transfer coefficient of these
72 membranes during the MD process with deionised (DI) water feed were assessed. Additionally,
73 the desalination performance parameters including water flux and salt rejection of the fabricated
74 SBS membrane was compared to those of the commercial PTFE membrane during the MD
75 process with a synthetic saline feed. Finally, the feasibility of the electrospun SBS membrane for
76 seawater desalination was demonstrated during a long term MD experiment process using
77 seawater as the feed.

78 **2. Materials and methods**

79 **2.1. Preparation of the electrospun SBS membrane**

80 The SBS membrane was prepared from a polymer solution with the SBS concentration of 15
81 wt.% using the electrospinning method. Linear tri-block SBS copolymer (C540 Calprene,
82 Dyansol) was dissolved in a mixture of analytical grade tetrahydrofuran (THF, Sigma Aldrich)
83 and dimethylformamide (DMF, Sigma Aldrich) (i.e. with a volumetric ratio of 75/25) at room

84 temperature with the help of a magnetic stirrer (MST, VELP). The SBS solution was then
85 transferred to a commercial Luer-Lock syringe, fitted with a 22-Gauge metallic needle prior to
86 the electrospinning processing. The electrospinning process was conducted under an electric field
87 of 1.0 kV/cm generated by a high voltage source (Gamma High Voltage Research Inc.). During
88 the electrospinning process, a syringe pump (KDScientific) was used to continually feed the
89 polymer solution into the needle tip. Electrospun fibers were collected on a grounded metallic
90 plate, and at temperature and relative humidity of 21 ± 2 °C and $43 \pm 5\%$, respectively.
91 Subsequent to the electrospinning process, the fabricated membranes were stored at temperature
92 of 40 ± 1 °C and low pressure of 93 kPa in a temperature-controlled vacuum chamber (Shel Lab,
93 Model 1410D) for at least 48 hours to completely remove any remaining solvent.

94 A commercially available PTFE (Porous Membrane Technology, Ningbo, China) was used to
95 bench-mark our novel SBS membrane. Detailed characteristics of this PTFE membrane are
96 available elsewhere [29].

97 **2.2. Membrane characterisation**

98 *2.2.1. Membrane surface morphology*

99 Morphology of the SBS and PTFE membranes was characterised using a low vacuum
100 scanning electron microscopy (SEM) (i.e. JSM-6490LV provided by JOEL, Japan) and atomic
101 force microscopy (AFM). Prior to SEM analysis, the membrane samples were coated with a thin
102 layer of gold using a sputter coater (Smart Coater, JEOL). Subsequent to SEM analysis, the fiber
103 diameters and their distribution of the two membranes were determined using ImageJ software
104 [30]. AFM imaging was conducted in non-contact mode and under room conditions using silicon
105 probes (Dimension 3100 Scanning Probe Microscope, Bruker) to evaluate surface roughness of
106 the membrane samples. **Three membrane locations ($10 \times 10 \mu\text{m}^2$) were randomly selected for**
107 **scanning**. The average membrane mean surface roughness (R_a) was then calculated using the
108 NanoScope Analysis software.

109 *2.2.2. Membrane porosity, pore size, and pore size distribution*

110 The porosity (ε) of the membrane samples was obtained using the pycnometer method [26,
111 31], and was calculated as:

$$112 \quad \varepsilon = \frac{(W_2 - W_3 - W_s)}{W_1 - W_3} \quad (1)$$

113 where W_1 , W_2 , W_3 , and W_s were the weight of the pycnometer filled with absolute alcohol, the
114 pycnometer filled with absolute alcohol and the immersed sample, the pycnometer without the
115 saturated sample, and the dry membrane sample, respectively.

116 A capillary flow porometry (Porolux 1000) was used to determine the pore size and pore size
117 distribution of the fabricated electrospun SBS and commercial PTFE membrane samples.
118 Detailed description of the method used is provided elsewhere [32].

119 2.2.3. Membrane surface hydrophobicity and liquid entry pressure

120 The surface hydrophobicity of the membranes was evaluated using water-membrane contact
121 angle measurements. The contact angle of the membranes was measured by the sessile drop
122 method using a Rame-Hart Goniometer (Model 250, Rame-Hart, Netcong, New Jersey, USA)
123 with deionised (DI) water as a reference. DI water droplets (12 μL) were deposited on the
124 membrane and the contact angles between the droplets and the membrane surface were
125 determined. A temperature-controlled chamber (Model P/N 100-07) was integrated with the
126 Rame-Hart Goniometer to facilitate the measurements of contact angle at different temperatures
127 (e.g. 25, 50, 55, and 60 $^{\circ}\text{C}$). [After placing the membrane inside the chamber, the temperature of
128 the chamber was increased to a desired value and stabilised for 5 minutes. A drop of water was
129 then placed on top of the membrane and the contact angle was recorded within 60 seconds.](#) At
130 least 5 droplets were deposited at different locations of each membrane sample for contact angle
131 measurement.

132 Liquid entry pressure (*LEP*) of the membrane was determined using a custom-made apparatus
133 [\(Supplementary Data, Fig. S1\)](#). The *LEP* apparatus consisted of a cylindrical cell connected with
134 a nitrogen gas bottle [33]. The cylindrical cell had a movable silicon base. DI water was filled
135 into the cell, then a dry membrane sample (i.e. effective surface area of 7 cm^2) was secured to the
136 cell on the top of water to form a chamber. The pressure caused by nitrogen gas at the bottom of
137 the water-filled chamber pushed the silicone base and water against the membrane. The nitrogen
138 gas pressure was increased stepwise. The applied pressure at which the first water bubble
139 appeared on the top membrane surface was recorded as the *LEP* value of the membrane.
140 Triplicate measurements were conducted for each membrane sample.

141 2.2.4. Membrane mechanical strength

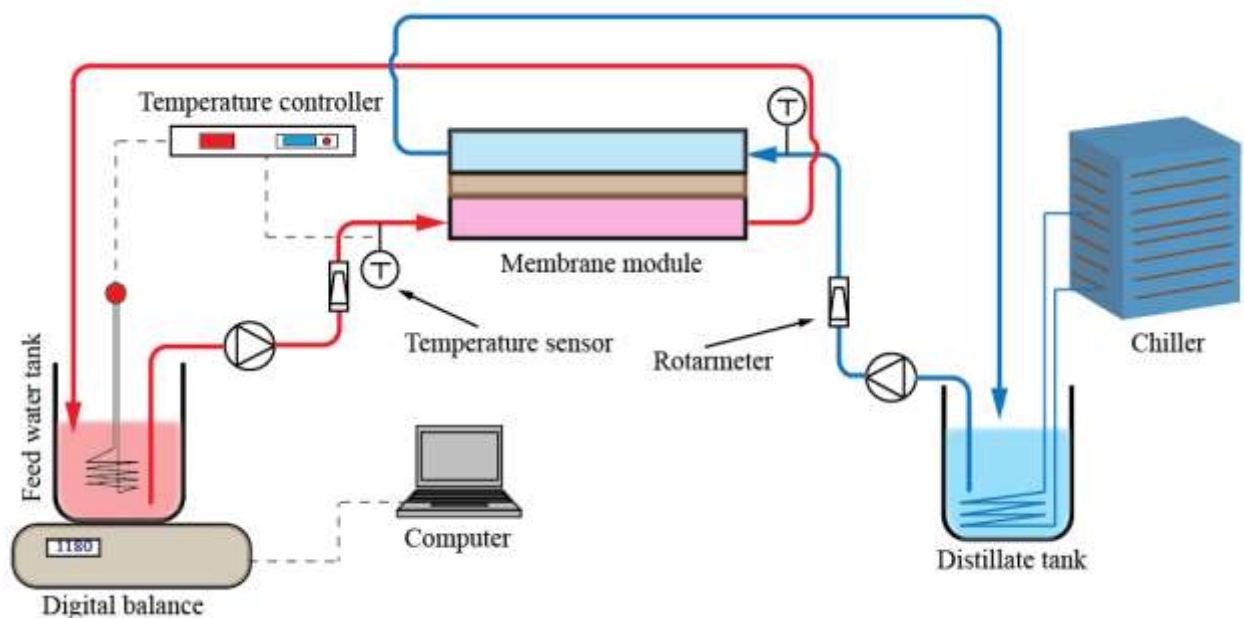
142 Stress-strain measurements were performed to assess the mechanical strength of the
143 fabricated SBS and commercial PTFE membranes. The measurements were conducted at 25 $^{\circ}\text{C}$
144 using a Shimadzu Universal Testing Machine (EZ-SX) with a 10 N load cell in tensile mode, and

145 at a strain rate of 1 mm/min. Rectangular stripes (i.e. with a size of $10 \times 40 \text{ mm}^2$) were measured
146 with a caliper (Mitutoyo) and a thickness (SBS = $200 \mu\text{m}$ and PTFE = $300 \mu\text{m}$) was measured
147 with a DUALSCOPE® MPOR (Fischer). From the stress-strain data, elastic modulus was
148 calculated in the linear zone, between 0 and 2% of strain, for all the samples. The ultimate tensile
149 strength and the strain-at-failure were also determined. The stress-strain measurements were
150 performed using five different specimens.

151 2.3. Membrane distillation performance evaluation

152 A lab-scale **direct contact** MD system (**Fig. 1**) was used to assess the distillation performance
153 (e.g. water flux, mass transfer coefficient, and salt rejection) of the fabricated SBS and the
154 commercial PTFE membranes for comparison purposes. The test system consisted of a plate-and-
155 frame MD membrane module and hot feed and cold distillate cycles. The membrane module
156 composed of two acrylic semi-cells; each cell was engraved to create a flow channel with depth,
157 width, and length of 0.3, 4.5, and 9.0 cm, respectively. A membrane coupon was sandwiched
158 between the two semi-cells to form the feed and distillate channels.

159 Feed water in the MD feed tank was heated using a submerged heating element connected to a
160 temperature control unit. A chiller with heat-exchanging coils submerged directly into the
161 distillate tank was used to control the distillate temperature. Two variable-speed gear pumps
162 (Model 120/IEC71-B14, Micropump Inc.) were used to circulate the feed and distillate through
163 the membrane module. A digital balance (PB32002-S, Mettler Toledo, Inc.) connected to a
164 computer was used to weigh the mass of the feed tank and determine the water flux.



165

166 **Fig. 1.** The schematic diagram of the MD test unit.

167 DI water, synthetic NaCl solution, and pre-filtered seawater were used as feed solutions. DI
168 water (i.e. with electrical conductivity of 40 $\mu\text{S}/\text{cm}$) was obtained from a Milli-Q water
169 purification system (Millipore). Analytical grade NaCl was dissolved in DI water to prepare the
170 synthetic solution. Seawater from Wollongong beach (New South Wales, Australia) was pre-
171 filtered by 0.5 μm filter papers. The pre-filtered seawater had conductivity, pH, and total
172 dissolved solids of 51.5 mS/cm, 8.32, and 35 g/L, respectively. The total organic carbon (TOC)
173 concentration of this pre-filtered seawater was negligible (<2 mg/L) [34].

174 The MD process with DI water was conducted to evaluate the water transfer through the
175 membranes. DI water feed at temperatures of 50, 55, and 60 $^{\circ}\text{C}$ was circulated through the feed
176 channel at a rate of 0.5 L/min (i.e. equivalent to cross-flow velocity of 0.06 m/s). DI water (4 L)
177 was used as initial distillate, and was circulated through the distillate channel at the same rate to
178 the feed. The distillate temperature was maintained constant at 20 $^{\circ}\text{C}$. Water flux of the process at
179 each feed temperature was recorded for two hours after the attainment of stable conditions. The
180 mass transfer coefficient (K_m) of the MD system was determined following the method described
181 by Duong et al. [35].

182 The MD process with synthetic NaCl solution and pre-filtered seawater feeds was
183 experimented to test the desalination efficiency (e.g. water flux and salt rejection) of the
184 membranes. The operating conditions were similar to those described above. During the
185 experiments, the obtained distillate was returned to the feed tank to maintain a constant feed
186 salinity. The electrical conductivity of the feed and distillate was measured with a conductivity
187 meter (Orion Star A322, ThermoFisher). The salt rejection ($S_{rejection}$) of the membranes was
188 calculated using Eq. 2 [given the negligible salt concentration of the initial distillate \[16, 36\]](#):

$$189 \quad S_{rejection} = \left(1 - \frac{EC_{distillate}}{EC_{feed}} \right) \times 100\% \quad (2)$$

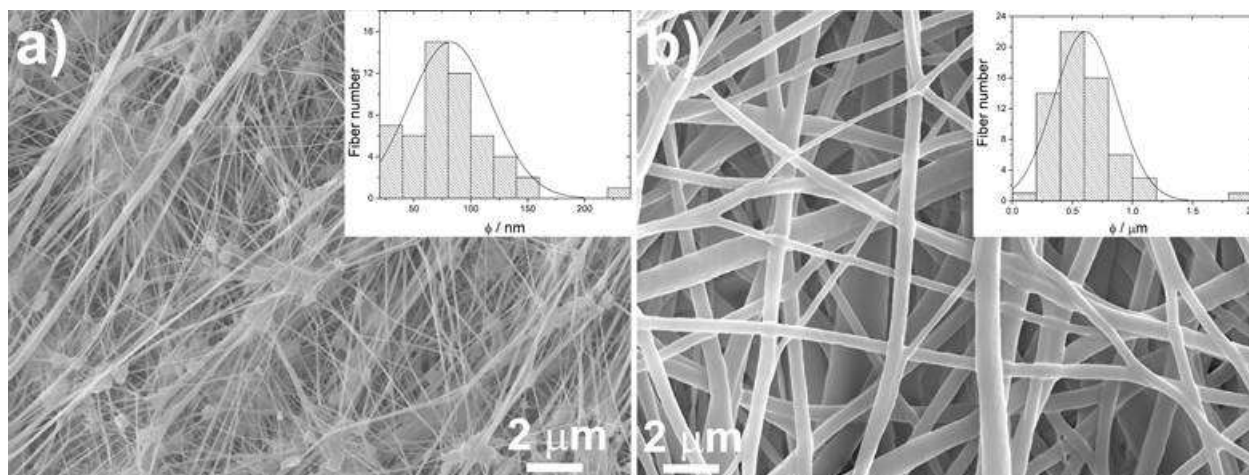
190 where $EC_{distillate}$ and EC_{feed} were electrical conductivity of the distillate and the feed, respectively.
191 [For the MD experiments with the synthetic NaCl solution feed, the feed and distillate](#)
192 [conductivities were measured 2 hours after the water flux has been stabilised.](#)

193 **3. Results and discussions**

194 **3.1. Membrane characterisation**

195 *3.1.1. Membrane morphology*

196 SEM images confirmed that the fabricated SBS membrane exhibited a microporous structure
197 similar to that of the PTFE membrane (**Fig. 2**). Both the SBS and PTFE membrane had micro
198 pores formed by interconnected fibers on their surfaces. The SBS membrane had a mean pore
199 size of 0.58 μm whereas that of the PTFE membrane was 0.46 μm . However, the SBS membrane
200 was composed of larger fibers (**Fig. 2**); thus, it exhibited a slightly lower porosity compared to
201 the PTFE membrane (i.e. 81% compared to 85%).



202 **Fig. 2.** Morphology of (a) the commercial PTFE membrane and (b) the fabricated SBS
203 membrane. The insets present the fiber diameters distribution of the membrane samples.
204

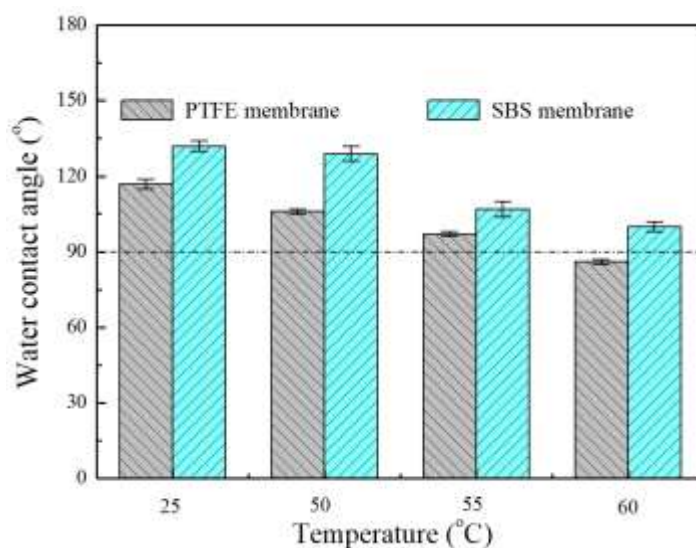
205 The difference in fiber diameters and pore sizes led to a notable difference in the surface
206 roughness between the fabricated SBS and commercial PTFE membranes. The SBS membrane
207 exhibited a surface roughness of 457.4 ± 36.5 nm, considerably rougher than PTFE membrane
208 surface (surface roughness of 235.4 ± 38.2 nm). Consistent with the SEM images, while the AFM
209 image of the PTFE membrane revealed randomly aligned fibers with small diameters, the SBS
210 membrane surface was composed of significantly larger fibers (Supplementary Data, **Fig. S2**).
211 Large fibers together with large voids between individual fibers rendered the higher surface
212 roughness of the SBS membrane compared to that of the PTFE one.

213 SEM micrographs of the membrane cross section showed the SBS membrane thickness of
214 200 μm , which is four times thicker than the active layer of the PTFE membrane. A thicker
215 membrane exhibits lower water flux but higher thermal efficiency due to a reduced heat loss via

216 conduction through the membrane [4, 6]. The comparison in water flux of the MD process with
217 the SBS and the PTFE membrane is discussed in the section 3.2.

218 3.1.2. Membrane wettability

219 The wettability of the membrane during the MD process depends on membrane properties
220 (e.g. surface hydrophobicity and membrane pore size) and operating conditions. The membrane
221 wettability can be assessed using water-membrane contact angle and liquid entry pressure (*LEP*).
222 The contact angle measurements demonstrated the superior surface hydrophobicity of the
223 fabricated SBS over the commercial PTFE membrane. At room temperature, while the PTFE
224 membrane exhibited a contact angle of $117 \pm 2^\circ$, that value of the fabricated SBS was $132 \pm 2^\circ$
225 (**Fig. 3**). Increasing temperature led to a decline in the contact angles of both PTFE and SBS
226 membranes. It is, however, noteworthy that as the temperature reached 60°C , while the SBS
227 membrane surface remained hydrophobic with a contact angle of 100° , the hydrophobicity of the
228 PTFE membrane had been significantly deteriorated (i.e. with contact angle $< 90^\circ$) (**Fig. 3**). The
229 decline in the membrane surface hydrophobicity with increased temperature can be attributed to
230 the decreased water surface tension [37, 38] and changes in the membrane morphology [38].



231
232 **Fig. 3.** Water contact angle of the commercial PTFE and the fabricated SBS membranes at
233 various temperatures. DI water was used as the reference liquid. Error bars represent standard
234 deviations of 50 measurements.

235 The SBS membrane had a lower *LEP* as compared with the commercial PTFE membrane
236 despite a higher surface hydrophobicity as discussed above. The *LEP* of the SBS membrane was
237 less than a half of that of the PTFE membrane (i.e. 81.0 ± 0.6 kPa compared to 192.0 ± 0.9 kPa).
238 The difference between the *LEP* of the fabricated SBS and commercial PTFE membranes can be

239 attributed to the difference in their pore size and pore structure. *LEP* depends on membrane pore
240 size and structure and membrane surface hydrophobicity as expressed in Eq. 3:

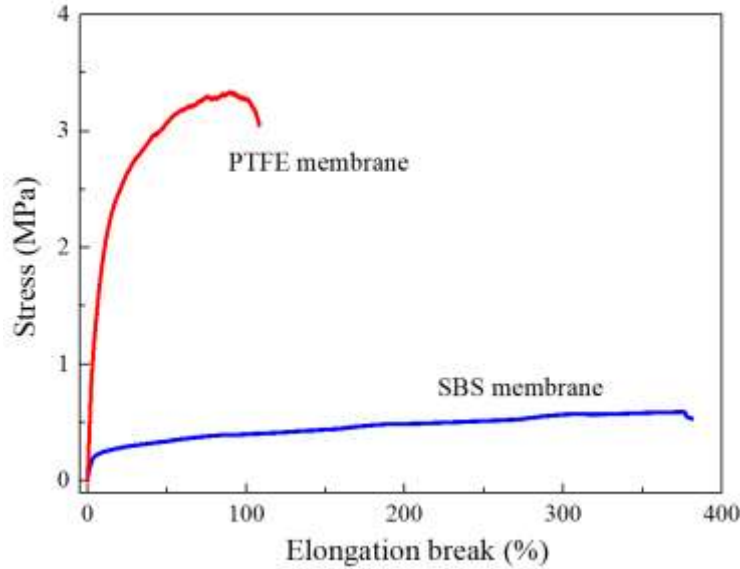
$$241 \quad LEP = \frac{-2B\gamma_l \cos \theta}{r_{\max}} \quad (3)$$

242 where *B* is a factor representing the geometry of the pores, γ_l is liquid surface tension, θ is the
243 contact angle of the membrane, and r_{\max} is the maximum membrane pore size. The fabricated
244 SBS membrane had a higher contact angle, but its maximum pore size was much larger (i.e. 1.55
245 μm compared to 1.12 μm); thus, it demonstrated a lower *LEP* compared to the PTFE membrane.
246 It is worth noting that the fabricated SBS membrane is compatible with MD applications with
247 respects to membrane wetting resistance. Indeed, the *LEP* value of most commercially available
248 flat-sheet MD membranes varies in a wide range from 48 to 463 kPa, depending on membrane
249 material and fabrication methods used [39].

250 3.1.3. Membrane mechanical strength

251 The stress-strain measurement results demonstrated higher mechanical strength of the SBS
252 membrane compared to the PTFE membrane (**Fig. 4**). The SBS samples underwent yielding,
253 necking and strain hardening when the strain was increased. During the initial mechanical
254 loading, the SBS fibers started rotating and aligning in the direction of the applied stress,
255 followed by a necking formation. At higher strain, an increase of the fiber alignment in the
256 direction of the mechanical load, which led to an increase of the stress recorded and was followed
257 by void growth, induced softening. As a result, the SBS membrane exhibited a maximum stress
258 and strain of 525 ± 50 kPa and $345 \pm 30\%$, respectively, and an elastic modulus of 9.8 ± 0.7 MPa.
259 On the other hand, the commercial PTFE membrane was more brittle with maximum stress and
260 strain of 3300 ± 230 kPa and $101 \pm 15\%$, respectively, and an elastic modulus of 37.2 ± 6.1 MPa
261 (**Fig. 4**).

262 It is noted that the mechanical strength of the fabricated membranes is lower than that
263 reported for bulk SBS material [40]. This can be attributed to the considerably lower density
264 (higher porosity) of the membrane samples as compared to bulk SBS material. Furthermore, in
265 the SBS membrane samples, the fibers are arranged in a nonwoven fashion and only a portion of
266 them contribute to the resistance to the applied mechanical loading, hence resulting in fewer
267 chain entanglements per unit of mass of the porous membrane as compared to the bulk SBS
268 material.

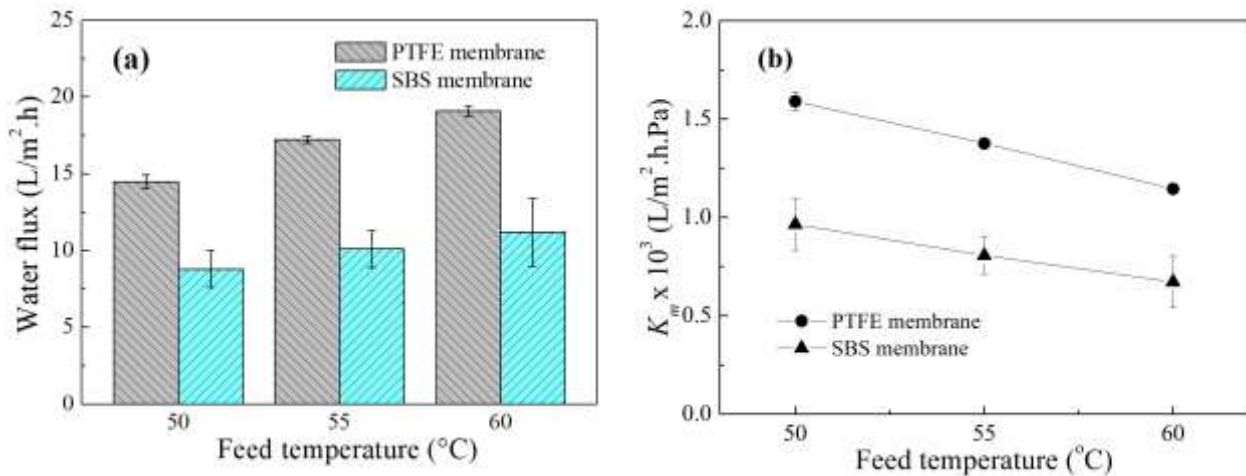


269
270 **Fig. 4.** Stress-strain curves of the fabricated SBS and commercial PTFE membranes.

271 **3.2. MD performance**

272 *3.2.1. Water flux*

273 The MD process with the SBS membrane achieved lower water flux than that with the
274 commercial PTFE membrane when DI water was used as the feed (**Fig. 5a**). The lower water flux
275 of the SBS membrane was mostly due to its higher thickness as compared to the commercial
276 PTFE membrane. Indeed, the thickness of the SBS membrane was two times of that of the PTFE
277 membrane. It is well-established that water flux of the MD process is inversely proportional to
278 the membrane thickness due to increased membrane resistance to the transfer of water vapour [4,
279 6]. Lower porosity of the SBS membrane is also a factor limiting its water flux when comparing
280 to the PTFE membrane.



281 **Fig. 5.** (a) Water flux and (b) mass transfer coefficient (K_m) as functions of operating feed
282 temperature during the MD process using the PTFE membrane and the fabricated SBS membrane
283 with the DI water feed. Operating conditions: feed and distillate circulation rates of 0.5 L/min
284 (i.e. cross flow velocities of 0.06 m/s), distillate temperature of 20 °C. The error bars represent
285 the standard deviation of five measurements.

286 The analysis of the process mass transfer coefficient (K_m) demonstrated a less severe
287 temperature polarisation effect of the MD process with the SBS membrane compared to that with
288 the PTFE membrane. The determination of K_m involved the temperatures in the bulk feed and
289 distillate streams instead of at the membrane surfaces; therefore, temperature polarisation effect
290 was embedded in K_m [35, 41]. Elevating feed temperature increases water flux and hence
291 exacerbates the temperature polarisation effect [42, 43]. As a result, the K_m values of the process
292 with both SBS and PTFE membranes decreased when the feed temperature increased (**Fig. 5b**).
293 However, K_m of the process with the SBS membrane decreased at a slightly lower rate than that
294 of the process with the PTFE membrane (**Fig. 5b**).

295 3.2.2. Desalination performance

296 Desalination efficiency (i.e. water flux and salt rejection) of the two membranes was
297 compared during the MD process with NaCl solutions. Given its lower K_m , water flux of the MD
298 process using the SBS membrane was lower than that of the process with the PTFE membrane
299 under the same operating condition (e.g. feed salinity, feed and distillate temperatures). In
300 addition, the process water flux from both the SBS and PTFE membranes decreased when the
301 feed salinity increased from 1 to 105 g/L as NaCl. This observed decrease in the process water
302 flux can be attributed to two factors: decreased feed water activity (i.e. colligative property of the
303 feed) and polarisation effects.

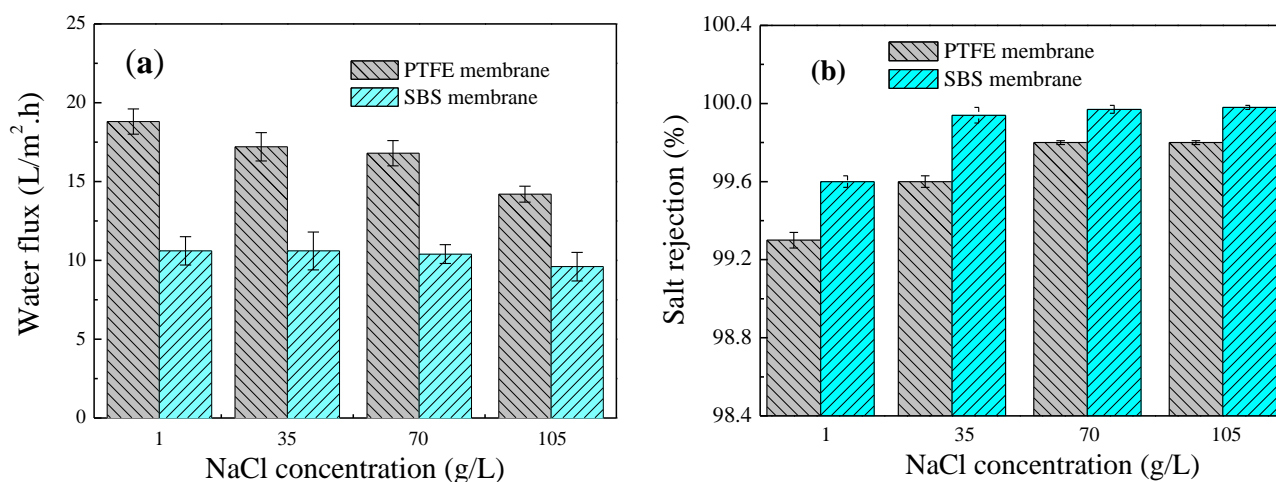
304 Increasing feed salinity reduces the feed water activity, and hence results in a lower water
305 vapour pressure of the feed stream, thus reducing the process water flux [4, 7]. For a dilute
306 solution, the effect of feed water activity on water vapour pressure can be estimated as [6]:

$$307 \quad P = x_{water}(1 - 0.5 \times x_{salt} - 10 \times x_{salt}^2)P_o \quad (4)$$

308 where P_o is the water vapour pressure of pure water; x_{water} and x_{salt} are the molar fraction of water
309 and salts, respectively. Based on Eq. (4), as the feed salinity increases from 1 to 105 g/L, the
310 water vapour pressure decreases by only 3%. Thus, polarisation appears to play a much more
311 significant role in this study.

312 The concentration polarisation effect was expected to be negligible when 1 g/L NaCl solution
313 was used as the feed. As the feed salinity increased, concentration polarisation became more

314 significant and temperature polarisation was also exacerbated due to the increase in feed
 315 viscosity. Therefore, water flux of the MD process decreased faster as the feed salinity increased
 316 beyond 70 g/L, especially for the commercial PTFE membrane (**Fig. 6a**). In comparison to the
 317 PTFE membrane, water flux from the SBS membrane was relatively stable when the feed salinity
 318 increased from 1 to 70 g/L (**Fig. 6a**). This is because the SBS membrane had a lower water flux
 319 and hence was less affected by concentration and temperature polarisation effects [4, 12].



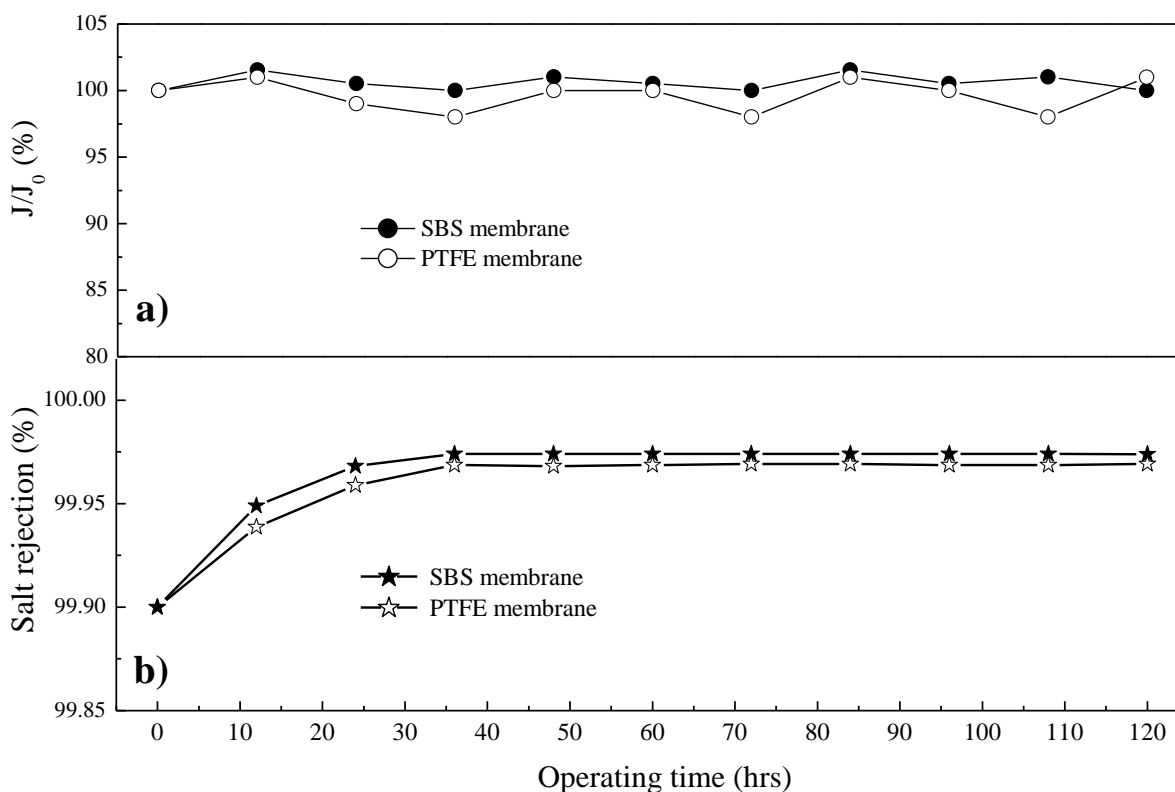
320 **Fig. 6.** Water flux and salt rejection of the fabricated SBS and PTFE membranes during the MD
 321 process with the synthetic NaCl solution feed at different feed salinity. Other operating
 322 conditions: feed temperature of 60 °C, distillate temperature of 20 °C, feed and distillate
 323 circulation rates of 0.5 L/min (i.e. cross flow velocities of 0.06 m/s). The error bars represent the
 324 standard deviation of five measurements.

325 The MD process with the SBS membrane achieved a higher salt rejection than that with the
 326 PTFE membrane at all NaCl concentrations (**Fig. 6b**). This is consistent with the higher surface
 327 hydrophobicity and roughness of the SBS membrane compared to those of the PTFE membrane.
 328 Indeed, improved salt rejection associated with enhanced membrane hydrophobicity and
 329 roughness has been reported in previous studies [27, 44]. **Increased membrane surface**
 330 **hydrophobicity and roughness result in a more efficient insulation layer between the liquid and**
 331 **membrane surface, thus limiting the intrusion of salt into the membrane pores** [27, 44]. The
 332 superior salt rejection by the SBS membrane is particularly useful for the separation of high value
 333 minerals such as in liquid desiccant regeneration for air conditioning systems [29] or the recovery
 334 of these minerals from diluted brines [45].

335 Long-term performance of the SBS and commercial PTFE membranes was demonstrated
 336 using pre-filtered seawater. During the MD process with the pre-filtered seawater feed, the
 337 produced distillate was returned to the feed tank to maintain a constant feed salinity (i.e. 35 g/L).

338 After 120 hours of continuous operation, water flux of the MD process using SBS and PTFE
 339 membrane remained constant (**Fig. 7a**). No evidence of membrane fouling or scaling was
 340 observed at the end of the experiment.

341 The observed salt rejection also confirmed the absence of membrane fouling during the MD
 342 process with the pre-filtered seawater feed using the SBS and PTFE membranes. Salt rejection by
 343 both the SBS and PTFE membranes gradually increased over the first 35 hours of the operation,
 344 then stabilised at 99.97% until the end of the long-term experiment (**Fig. 7b**).



345 **Fig. 7.** Normalised water flux (J/J_0) and salt rejection during the MD process of pre-filtered
 346 seawater feed. Operating conditions: feed temperature of 60 °C, distillate temperature of 20 °C,
 347 feed and distillate circulation rates of 0.5 L/min (i.e. cross flow velocities of 0.06 m/s). The
 348 salinity of the seawater feed was maintained constant by returning the distillate back to the feed
 349 tank throughout the experiments.
 350

351 3.3. Feasibility consideration

352 The summary of the membrane characteristics and distillation performance of the SBS and
 353 PTFE membrane is provided in **Table 1**. This new SBS membrane is superior to the commercial
 354 PTFE membrane with respect to mechanical properties and surface hydrophobicity. The SBS
 355 membrane exhibits a noticeably lower elastic modulus than the PTFE membrane given the
 356 presence of soft monomeric units in SBS. On the other hand, both membranes are comparable in

357 terms of porosity. The higher surface roughness and the superior surface hydrophobicity,
 358 especially at high temperatures, also induces higher salt rejection for the SBS membrane as
 359 compared to the PTFE one. Improved salt rejection and resistance to polarisation effects are
 360 possibly crucial to the MD applications for regeneration of hyper saline solutions such as liquid
 361 desiccant solution or forward osmosis draw solution. Nevertheless, further improvement is
 362 required to improve the water flux of the SBS membrane, which was considerably lower
 363 compared to the commercial PTFE membrane. The observed low water flux by the SBS
 364 membrane is attributed to its significantly higher membrane thickness (hence higher membrane
 365 mass transfer resistance). SBS is a soft elastomer; thus, a thick electrospun SBS layer is required
 366 to produce flat sheet membrane for MD operation. It is envisioned that by producing a thin film
 367 composite membrane in which a supporting layer can be used to provide the mechanical stiffness
 368 to prevent curving can potentially be used to address this issue in a future study.

369 Overall, the SBS membrane promises to be a strong competitor for the PTFE membrane
 370 concerning the membrane production and disposal costs. Raw SBS is biodegradable and more
 371 affordable than PTFE – the fabrication of the SBS membrane involves only a single
 372 electrospinning step and low cost raw materials, while the PTFE membrane manufacturing
 373 entails complicated multi-stage processes with costly raw materials and toxic additives. The
 374 biodegradability of the SBS membrane also helps to negate the disposal issues when MD
 375 membrane modules are disposed at the end of their lifetime.

376 **Table 1.** Comparisons between the commercial PTFE and the fabricated SBS membrane.

Sample	Porosity (%)	Thickness (μm)	Mean pore size (μm)	Roughness (nm)	Contact angle ^a (°)	E^b (MPa)	Flux ^c ($\text{L}/\text{m}^2\cdot\text{h}$)
PTFE membrane	85 ± 10	100 ± 7	0.46	235.4 ± 38.2	117 ± 2	37.2 ± 6.1	19.1 ± 0.3
SBS membrane	81 ± 4	200 ± 15	0.58	457.4 ± 36.5	132 ± 2	9.8 ± 0.7	11.2 ± 2.2

^a with DI water at 25 °C

^b elastic modulus

^c with DI water feed and operated at feed and distillate temperature of 60 and 25 °C, water circulation rate of 0.5 L/min

377 4. Conclusions

378 A novel hydrophobic, microporous membrane based on styrene-butadiene-styrene (SBS)
 379 polymer was prepared using the electrospinning method. The SBS membrane was systematically
 380 evaluated in comparison to a commercial polytetrafluoroethylene (PTFE) membrane. The SBS
 381 membrane had larger membrane pore sizes and fiber diameters but comparable membrane
 382 porosity compared to the PTFE one. The fabricated SBS membrane was two times thicker, and
 383 thus had a lower water flux than the PTFE membrane. Nevertheless, the SBS membrane showed

384 better salt rejection, higher surface hydrophobicity and superior mechanical strength over the
385 reference PTFE membrane. The high membrane surface hydrophobicity prevented the intrusion
386 of liquid into the membrane pores, thus improving the salt rejection of the SBS membrane. The
387 SBS membrane showed stable water flux and excellent salt rejection (i.e. >99.97%) throughout a
388 long term MD operation using seawater as the feed. The results from this study reveal great
389 potential of SBS as a promising alternative to conventional MD membrane materials for
390 desalination applications.

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