Facile development of comprehensively fouling-resistant and self-cleaning high performance aliphatic polyketone-based thin film composite forward osmosis membrane for treatment of oily wastewater

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Abstract

Forward osmosis (FO) has proven to be a suitable process for treatment of problematic oily wastewater, due to its relatively higher water recovery rate and lower energy requirement, as opposed to pressure-driven membrane processes. Despite the lower membrane fouling propensity during FO operation, the development of comprehensively fouling-resistant and self-cleaning membranes are further desired in FO as a suitable oily wastewater treatment process. In this study, thin film composite (TFC) membranes were developed using reduced aliphatic polyketone (rPK) as the membrane substrate, on which a thin polyamide active layer was formed via interfacial polymerization. Reduction conditions using $NaBH_4$ were tested, and the suitability of reduction was evaluated in terms of membrane morphology, water wettability, and resistance to oil. The resultant rPK-TFC membrane, whose substrate was reduced with 0.5% (w/w) $NaBH_4$ for 10 min, exhibited a water flux of 37.8 L m^{-2} h^{-1}, when tested in PRO mode. Using a foulant solution containing 1% (v/v) soybean oil, and 100 ppm bovine serum albumin, humic acid, and sodium alginate, the resultant rPK-TFC membrane maintained an outstanding 95% average flux recovery ratio, while the pristine PK-TFC membrane achieved an average flux recovery ratio of 67%. The results indicate that reduction of aliphatic polyketone is a facile method to develop membranes with outstanding water permeability, fouling resistance, and self-cleaning capability.

1. Introduction

Forward osmosis (FO) occurs through the transport of water through a semi-permeable membrane from a stream of lower solute concentration (feed solution, FS) to a stream of higher solute concentration (draw solution, DS). Water transport is mainly governed by the osmotic pressure (π) difference between the FS and the DS. This osmotically-driven membrane process does not require the application of hydraulic pressure, hereby offering the following advantages: sustainable water recovery potential, low fouling tendency, satisfactory contaminant rejection, and less energy consumption depending on chosen application [1]. FO can be applied for a number of applications, which include, but not limited to, desalination [2], resource recovery [3], juice dewatering [4], osmotic power generation [5, 6], and wastewater treatment [7].

Due to the wide applicability of FO, it can be a useful process to solve the current water scarcity and increasing demand for clean water, which is primarily caused by the exponential world's population growth and industrialization. Among the various applications of FO, wastewater treatment and reuse are particularly of extreme importance, since not only do these processes augment our usable water supply, issues concerning environmental pollution can also be mitigated [8].

Industrialization has brought about the world's dependency in the oil and gas industries, and this has led to the disposal of oil waste into water bodies without any prior treatment. Therefore, oily wastewater, which contains oil, dissolved organic and inorganic substances, and suspended solids, is a huge environmental concern. Not only can oily wastewater negatively affect aquatic life, it can also pose adverse effects on human health and agriculture [7].

FO, as mentioned above, is a suitable candidate in mitigation of the environmental impact of oily wastewater; however, the development of robust, highly selective, and fouling-resistant

membranes for wastewater treatment-specific osmotic process is highly essential. Several studies have been done on polyamide-based thin film composite (TFC) membranes, which exhibit higher water permeability, higher selectivity, and satisfactory mechanical strength. Thus, in recent, various fabrication methods and membrane modification have been performed to further improve separation performance and fouling resistance. Among these FO membrane modification and fabrication methods include the incorporation of highly porous nano-sized fillers [9, 10], hydrophilic coating [11, 12], electrolyte deposition [13, 14], incorporation of zwitterionic substances [7, 15], and chemical grafting and modification [16, 17].

Chemical modification of polyketone is chosen as the approach for membrane development in this study. Ketones are known to be highly reactive compounds, but not as much as aldehydes which share the same carbonyl ($—(C═O)—$) group, primarily due to the presence of the less electrophilic secondary carbon (the carbonyl C atom is surrounded by two hydrocarbon groups). However, the high reactivity of ketone is mainly influenced by the presence of the carbon-oxygen double bond. Ketones are known to produce secondary alcohols after reduction with certain reducing agents such as $LiAlH_4$ and $NaBH_4$.

In this study, polyketone was reduced using $NaBH_4$ prior to interfacial polymerization. The suitability of reduction in preparation of TFC membranes was first determined, and the separation properties and comprehensive fouling resistance against model oil, protein, carbohydrate, and humics foulants were also evaluated. This study aims to provide evidence that a facile chemical modification of the TFC membrane substrate can significantly alter the membrane transport properties and enhance the fouling mitigation and self-cleaning capability during treatment of oily wastewater.

2. Experimental

2.1. Chemicals

Aliphatic polyketone ($M_w = 200\,000$ g mol^{-1}) provided by Asahi Kasei Co., Japan was chosen as the polymer for the membrane substrate. The following solvents and chemicals were used for membrane substrate casting: resorcinol (> 99.0 %, Tokyo Chemical Industry Co., Ltd., Japan), methanol (> 99.8 %, Fujifilm Wako Pure Chemical Corporation, Japan), acetone (> 99.8 %, Fujifilm Wako Pure Chemical Corporation, Japan), and hexane (> 99.8 %, Fujifilm Wako Pure Chemical Corporation, Japan). Reduction of the polyketone substrates was performed using sodium borohydrite (sodium tetrahydroborate, NaBH$_4$, powder, Fujifilm Wako Pure Chemical Corporation, Japan).

During interfacial polymerization, the following substances were used: *m*-phenylenediamine (MPD, Fujifilm Wako Pure Chemical Corporation, Japan), 1,3,5-benzenetricarbonyl trichloride (trimesoyl chloride, TMC, > 98.0 %, Tokyo Chemical Industry Co. Ltd., Japan), (±)-10-camphorsulfonic acid (CSA, > 98.0 %, Tokyo Chemical Industry Co. Ltd., Japan), triethylamine (TEA, > 99.0 %, Wako Pure Chemical Industries, Ltd., Japan), sodium dodecyl sulfate (SDS, Fujifilm Wako Pure Chemical Corporation, Japan), and heptane (> 99.3 %, Fujifilm Wako Pure Chemical Corporation, Japan).

For fouling resistance studies, the following model foulants were chosen: soybean oil (Wako, Fujifilm Wako Pure Chemical Corporation, Japan), bovine serum albumin (BSA, Wako Pure Chemical Corporation, Japan), humic acid (sodium salt, Sigma-Aldrich, Japan), and sodium alginate (Nacalai Tesque, Inc., Japan).

All the substances used in this study were used as received and without further treatment.

103

2.2. Membrane fabrication

2.2.1. Polyketone substrate casting and subsequent reduction

Polyketone (PK) substrate was prepared by conventional non-solvent-induced phase separation (NIPS) process, according to a previous study [18]. A 10 % (w/w) PK solution was prepared with 65 % (w/w) aqueous resorcinol as solvent. The solution was stirred at 80 °C for 3 h, and degassed at 50 °C overnight. The solution temperature was maintained at 50 °C prior to casting. The solution was poured on a glass plate and was spread using a stainless-steel casting knife with a casting thickness of 400 µm. The nascent PK substrate was afterwards immersed in a 35 % (w/w) aqueous methanol coagulation bath at 25 °C to allow complete phase separation and equipped in steel frames to avoid shrinkage. The substrates were afterwards washed with acetone and hexane successively for 20 min each and air-dried until further use.

Reduction of the PK substrate was performed by immersion of the PK membranes in 0.5% (w/w) aqueous $NaBH_4$ solution for a varied period of time (5 to 30 min), after which, the reduced membranes were washed with acetone and hexane successively for 20 min each, and air-dried until further use.

2.2.2. In situ interfacial polymerization and thin film composite membrane preparation

To prepare a PK-based TFC membrane, the selective polyamide layer was formed on one side of the pristine and reduced PK substrates through *in situ* interfacial polymerization described in a previous study [19]. An aqueous amine precursor solution, containing 2.0 % w/w MPD, 1.1 % w/w TEA, 2.3% w/w CSA, and 0.15 % w/w SDS, was first introduced onto one side of the PK substrate for 5 min. The excess solution was afterwards discarded, and the membrane substrate

126   was allowed to stand for 1 min. Air knife was afterwards used to remove the excess amine

127   precursor solution. An organic acyl halide precursor solution, containing 0.15 % w/w TMC in

128   heptane was introduced and made to react with the residual amine precursor for 2 min. The excess

129   acyl halide solution was removed, and the membrane was allowed to stand for 1 min, and

130   afterwards cured at 90 °C for 10 min to complete the reaction. The resultant TFC membrane was

131   washed with copious amounts of deionized (DI) water, stored in DI water, and placed in cool and

132   dark condition prior to testing and characterization.

133

134   ### *2.3. Determination of intrinsic transport parameters*

135   Pure water permeability (PWP, A, L m^{-2} h^{-1} bar^{-1}) and solute permeability (B, L m^{-2} h^{-1}) were

136   determined using a cross-flow reverse osmosis (RO) system with an effective membrane area (A_m)

137   of 8.04 cm^2, under a pressure of 10 bar, temperature of 25°C, and a flow rate of 150 mL min^{-1}

138   [20]. DI water and 1000 mg L^{-1} NaCl were used as a feed for determination of A and B, respectively.

139   The equations used for calculation of A and B were reported in a previous study [13].

140

141   ### *2.4. Membrane osmotic performance*

142   The osmotic performance of the TFC membranes were evaluated using a custom laboratory-

143   scale FO system [20], with a cell whose effective membrane area is 4.5 cm^2 and two peristaltic

144   pumps (NS Pump NPL-100, Nihon Seimitsu Kagaku Co., Ltd., Japan) delivering the feed and

145   draw solutions, originally 1 L in volume each. FO tests were conducted in two modes: AL-FS (FO

146   mode, active layer facing the feed solution) and AL-DS (PRO mode, active layer facing the draw

147   solution). The hydraulic pressures of both feed and draw were kept at minimum, and the flow rates

148   of the solutions were maintained at 3 x 10^{-1} L min^{-1}. The mass of the permeate was measured using

149   an electronic top-loading balance (FX-3000i, A&D Company, Limited, Japan) connected to a

150   computer. Reverse salt flux was evaluated through the change in feed solution conductivity

151   measured by a conductivity meter (LAQUAtwin, Horiba Ltd., Japan). Water flux (J_w) and reverse

152   salt flux (J_s) were calculated using equations presented in previous study [11].

153

154   ### *2.5. Fouling*

155   1% (v/v) soybean oil-in-water emulsion was first prepared by mixing together soybean oil,

156   water, and 0.01 ppm SDS surfactant, followed by constant stirring for 12 h. Three 1% (v/v)

157   soybean oil-in-water emulsions spiked with 100 ppm of BSA, humic acid, and sodium alginate

158   were also prepared. Individual fouling tests were conducted for 8 h, with the foulant solutions as

159   feed and 1.0 M NaCl as the draw, using the same FO system mentioned above. The concentration

160   of the draw solution was kept constant at 1.0 M by regular addition of NaCl to avoid dilution effect.

161   Total organic carbon analyzer (TOC-VCSH, Shimadzu Co., Japan) was used to measure the oil

162   concentration (C_O) in the DS. C_O, along with the volume of the draw solution (V), at time t is used

163   to calculate oil flux (J_O), as in **Eq. 1**:

164   $$J_O = \frac{C_O V}{A \Delta t} \tag{1}$$

165   A comprehensive fouling solution containing 1% (v/v) soybean oil, 0.05 ppm SDS, and 100

166   ppm each of BSA, humic acid, and sodium alginate was prepared. The membranes were tested for

167   fouling resistance with the comprehensive fouling solution as feed and 1.0 M NaCl as draw for 8

168   h, and then backwashed for cleaning with DI water, and tested for fouling again for another 8 h.

169   The water flux recovered after membrane cleaning, along with the initial water flux, was used to

170   evaluate the flux recovery ratio, which can be calculated as the ratio of the final and the initial

171   water flux values [21].

172

2.6. Membrane characterization

Membrane surface and cross-sectional morphology was characterized using field-emission scanning electron microscopy (FE-SEM, JSF-7500F, JEOL, Japan). The average surface pore size and pore size distribution were determined using SEM image analysis software (Nano Measurer 1.2). Measurements were done in triplicate.

Surface chemistry was characterized using Fourier transform infrared (FTIR) spectroscope (Nicolet iS5, Thermo Fisher Scientific, Japan) with an attenuated total reflectance detector (ATR; iD5, Thermo Fisher Scientific, Japan) and X-ray photoelectron spectroscopy (XPS, JPS-9010 MC, JEOL, Japan) with Al Kα X-rays.

The membrane hydrophilicity and oleophobicity were evaluated by an optical contact angle goniometer (Drop Master 300, Kyowa Interface Science Co., Japan) [22]. Water static contact angle measurements were obtained after dispensing a 4 µL water droplet onto the membrane sample. Underwater oil contact angle was determined using special J-shaped needles which release oil droplets upward. 10–15 µL oil droplets of soybean oil were contacted with the membrane.

3. Results and Discussion

3.1. Aliphatic polyketone reduction

Reduction of ketone (R—(C=O)—R') functional groups with common reducing agents, such as $LiAlH_4$ and $NaBH_4$ (used in this study), readily forms alcohol functional groups. As shown in **Scheme 1**, reduction of larger chain of ketone functional groups, such as polyketone, results to a partial reduction of the carboxyl groups into alcohol. The hydroxyl (—OH) groups of alcohol

195 readily forms H-bonds with water, thus increasing the overall hydrophilicity and the electrically-

196 neutrality of the polyketone membrane substrate [18].

197

Polyketone → (NaBH$_4$ or LiAlH$_4$) → **Reduced polyketone**

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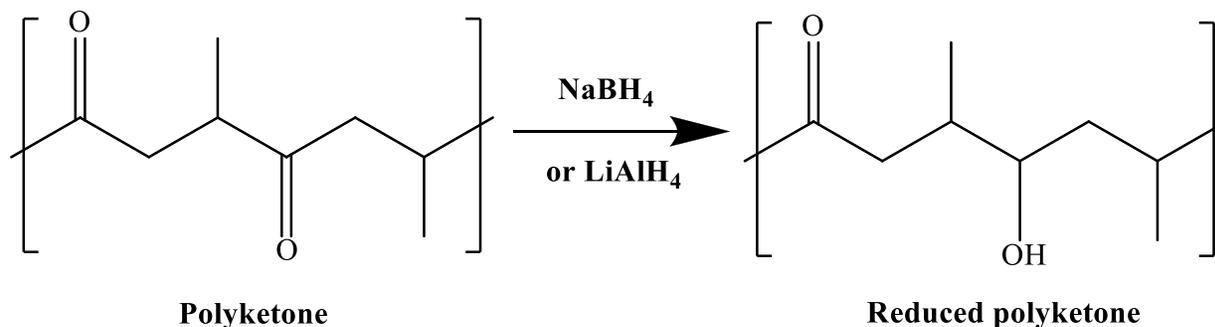
199 **Scheme 1**. The reduction of polyketone with NaBH$_4$ or LiAlH$_4$ as the reducing agents.

200

201   The morphology of the membranes was characterized using FE-SEM to determine the effect

202 of reduction on the morphology and the formation of defects, if ever. FTIR and XPS were used to

203 determine the success of the reduction of polyketone. The pristine polyketone substrate was first

204 reduced at 0.5% NaBH$_4$ at different reduction times of 5—30 min. **Figure 1** and **2** show the surface

205 morphology and surface chemistry of the pristine polyketone (PK-0) and the reduced polyketone

206 (rPK-1 to rPK-4, reduced at 5, 10, 20, and 30 min, respectively.

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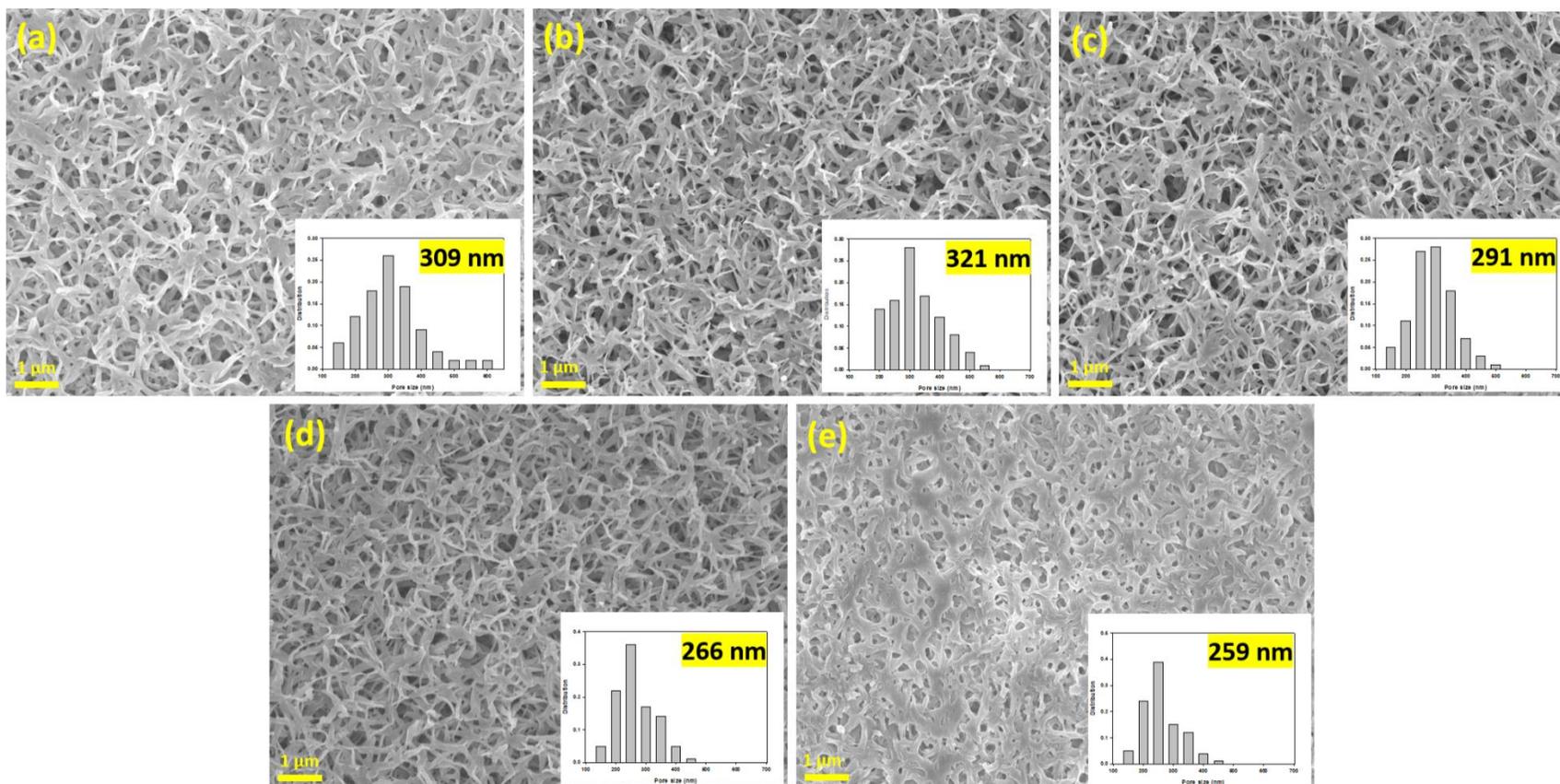
Figure 1. Surface morphology of (a) pristine polyketone (PK-0) and reduced polyketone substrates (rPK-1 to rPK-4) which were reduced at (b) 5, (c) 10, (d) 20, and (e) 30 min, respectively. Pore size and pore size distribution of the membrane substrates included inset).
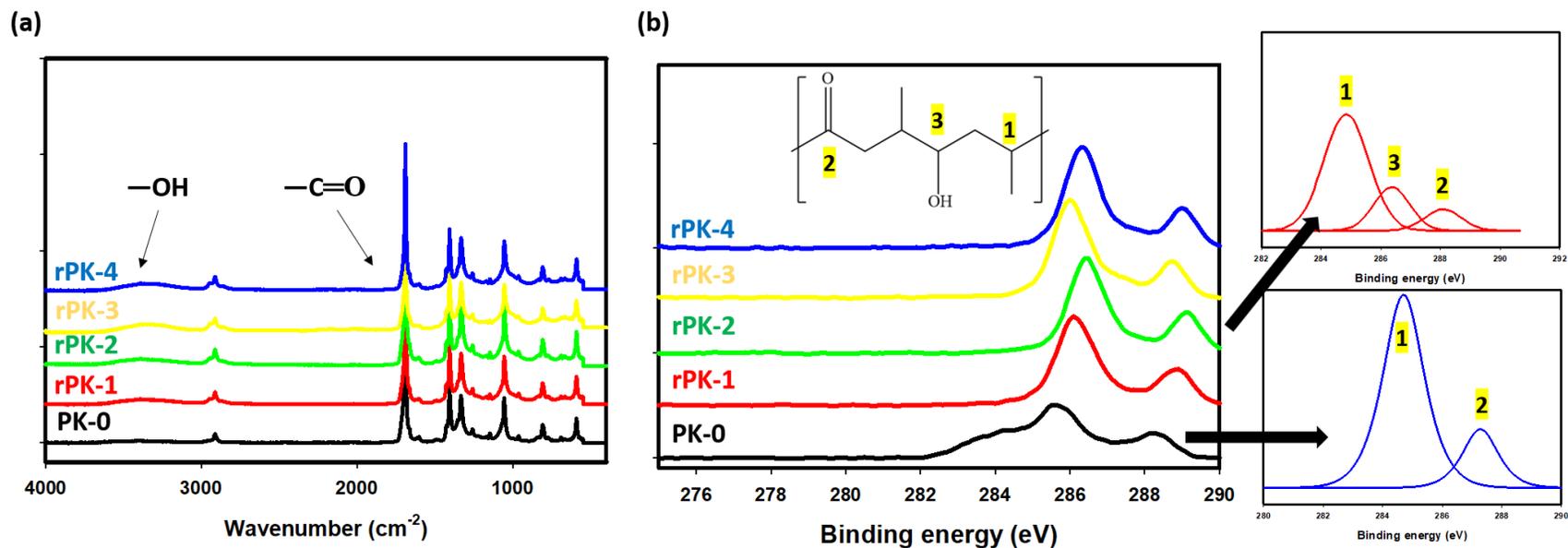
Figure 2. Surface chemistry of pristine polyketone (PK-0) and reduced polyketone substrates (rPK-1 to rPK-4) which were reduced at 5, 10, 20, and 30 min, respectively, as shown from the (a) FTIR spectra and (b) XPS C_{1s} spectra of the membrane substrates. The different carbon species are labeled accordingly: (1) C—C; (2) C=O; and (3) C—OH.

214　　　　The fibrous morphology of polyketone can be seen in all the samples; and the pore size

215　　　distribution indicates that there was no significant alteration in the pore size of the polyketone

216　　　substrate during reduction, but a significant marked decrease in pore size was observed with the

217　　　samples reduced for 20 and 30 min. While rPK-1 and rPK-2 maintained the highly porous structure

218　　　of pristine polyketone, this was not the case for the rPK-3 and rPK-4, which showed denser skin

219　　　layers after the chemical modification.

220　　　　The microporous structure of polyketone is interesting to investigate due to its highly

221　　　symmetric morphology all throughout, with interconnected fibrous structures distributed

222　　　uniformly all over the substrate. Ease in water permeability and mitigation of water transport

223　　　resistance are owed to the porous structure of polyketone. What is even more noteworthy is that,

224　　　unlike other membrane chemical modification processes, polyketone reduction does not

225　　　significantly alter the membrane's porous structure.

226　　　　Comparing the surface chemistry of the samples, both the FTIR and XPS spectra show that

227　　　the reduction of the carboxyl groups of the polyketone into alcohol took place. The pristine

228　　　polyketone substrate showed strong characteristic peaks at around 1050, 1400, and 1690 cm^{-1},

229　　　corresponding to the following respective groups: C—C, —CH$_2$—, and C=O [23]. The FTIR

230　　　spectra of the reduced polyketone substrates show a wide stretch at 3400 cm^{-1}, revealing the

231　　　presence of —OH and indicating the success of the partial polyketone reduction [18]. Until the

232　　　reduction time of 20 min, the amount of carboxyl groups on the outer surface of the membrane

233　　　reduced, or hydroxyl groups formed were found to increase as reduction time increases. After

234　　　reduction for 20 min, the surface chemistry of the reduced polyketone showed similar C$_{1s}$ spectra

235　　　and speciation. As seen in **Figure 2(b)**, the pristine polyketone substrate also has two species of

236　　　carbon present, the aliphatic carbon (around 284 eV) and the carbonyl carbon (around 288 eV).

237   After reduction, the rPK substrates exhibit the presence of carbon attached to the hydroxyl group

238   —OH (around 286 eV).

239   The pristine polyketone and reduced polyketone substrates were used for interfacial

240   polymerization to form TFC membranes. The TFC membranes prepared from rPK-3 and rPK-4

241   (reduced for 20 and 30 min, respectively) exhibited polyamide delamination instantaneously as the

242   membranes were placed in DI water right after interfacial polymerization. The delamination of the

243   polyamide active layer can be attributed to a number of factors, particularly, membrane substrate

244   porosity and hydrophilicity. After polyketone reduction at longer periods of 20 and 30 min, there

245   was an observed significant decrease in the substrate surface porosity. It is therefore highly likely

246   that the aqueous amine monomer precursor (MPD) was not able to fully impregnate the reduced

247   membrane substrate due to lower surface porosity. This then results to the formation of polyamide

248   layer with lower cross-linking degree and adhesion with the membrane substrate, and thus, it can

249   easily be removed from the membrane substrate [24]. When exposed in water, the polyamide

250   swells easily, and the polyamide swelling phenomenon undermines its mechanical stability as a

251   result of increased polymer bond distance and weaker chain segments [25]. In relation to the

252   swelling phenomenon, membrane substrate hydrophilicity also plays a huge part in delamination

253   of the polyamide active layer. Deposition of the polyamide active layer on top of the membrane

254   substrate is mainly governed by adhesion forces, and when the membrane substrate is highly

255   hydrophilic, the adhesive forces between the polyamide and the substrate become substantially

256   weaker [26]. The high hydrophilicity of the membrane substrate then allows water to enter the

257   interface of the polyamide and the substrate, resulting in swelling and delamination. For the rest

258   of this study, therefore, only the TFC membranes formed on PK-0, rPK-1, and rPK-2 were

259   considered.

260

3.2. Hydrophilicity and underwater oleophobicity

A particularly important aspect of this study is the influence of the chemical modification of polyketone on the material's hydrophilicity and underwater oleophobicity. These two properties are known to influence the membrane water permeability, and therefore, osmotic performance, and the fouling resistance, as well. **Figure 3** shows the water and underwater oil contact angle profiles of the pristine and reduced polyketone substrates.

Pristine polyketone exhibited a water contact angle of $54.2 \pm 2.8°$. As expected from the chemical modification procedure, the hydrophilicity of the substrates increased after reduction, as evidenced by the significant decrease in the water contact angles. Full penetration of the water droplet into the membrane substrate was achieved after 12 s. rPK-1 showed a water contact angle of $38.4 \pm 1.7°$, while rPK-2 has a water contact angle of $25.1 \pm 2.8°$. For both instances, the water droplet has fully penetrated on the membrane surface in less than 5 s, further indicating the enhanced hydrophilic nature of the reduced polyketone substrate.
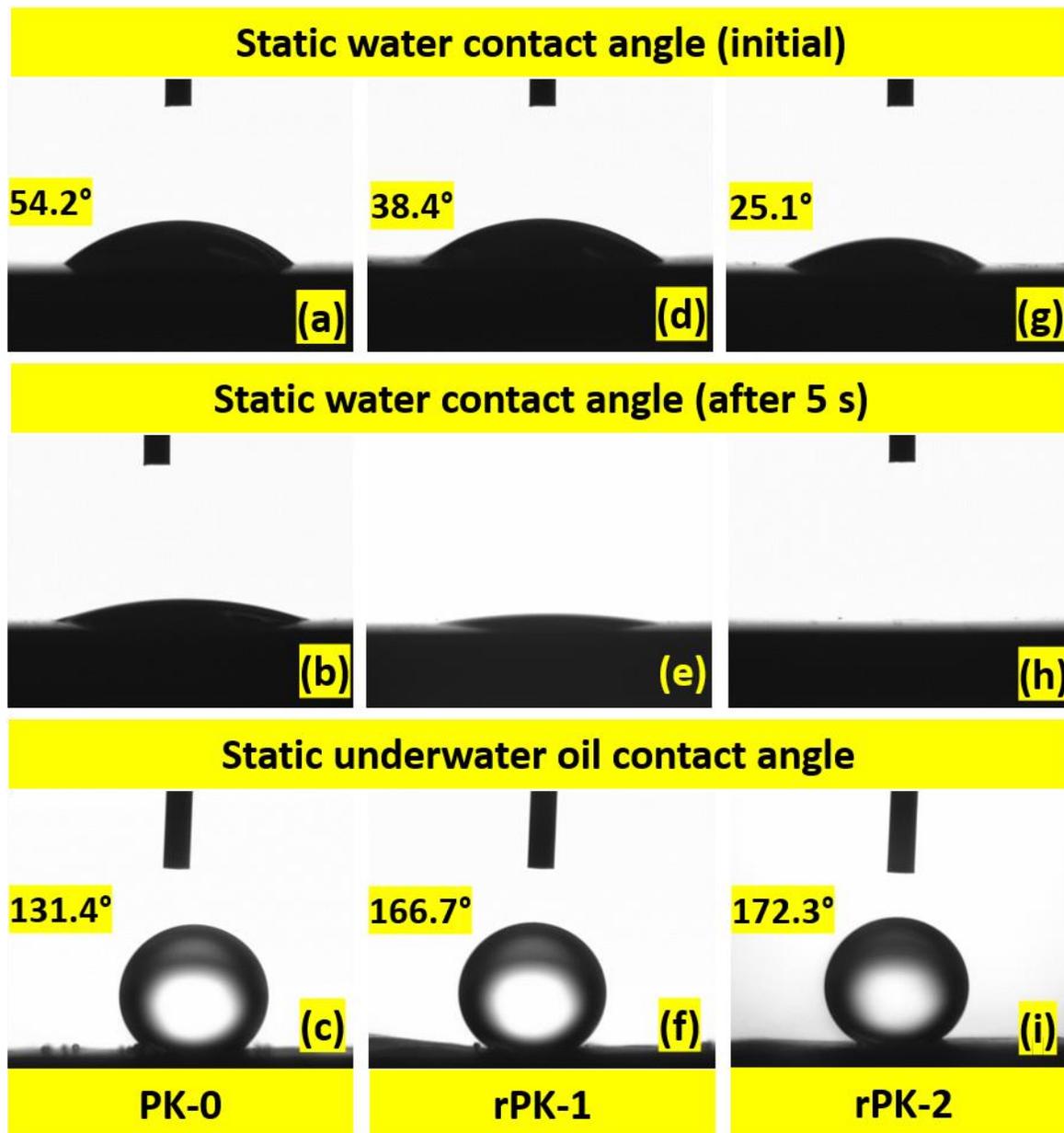
Figure 3. Hydrophilicity and underwater oleophobicity of the (a-c) pristine and reduced polyketone substrates, (d-f) rPK-1 and (g-i) rPK-2, as evidenced by the water contact angle and underwater oil contact angle. Soybean oil was used as the model oil for the underwater oleophobicity characterization.

279   The underwater oil contact angle, on the other hand, is a measure of the oleophobicity of the

280   membrane samples, such that a higher underwater contact angle indicates a higher degree of

281   oleophobicity. This particular parameter is influenced by the hydration layer surrounding the

282   membrane, such that, the strength of the hydration layer is directly proportional to the

283   oleophobicity (and oil contact angle). Pristine PK-0 substrate exhibited an underwater oil contact

284   angle of $131.4 \pm 3.9°$, which indicates that polyketone is fairly oleophobic. In the case of rPK-1

285   and rPK-2, both demonstrated outstanding oleophobicity with underwater oil contact angle values

286   of $166.7 \pm 4.8°$ and $172.3 \pm 3.8°$, respectively. It was also noticed that delivering the oil droplets

287   onto the reduced polyketone membrane surface required a higher volume of oil droplet to be

288   allowed to be released by the needle during characterization. It is also worth noting that the oil

289   droplets appeared to be stable on the reduced PK substrate surface even after 5 min. These

290   demonstrate the robust oil-repellant property of the reduced polyketone substrates.

(a) 68°

(b) 197 nm

(c) 63°

(d) 228 nm

(e) 61°

(f) 204 nm

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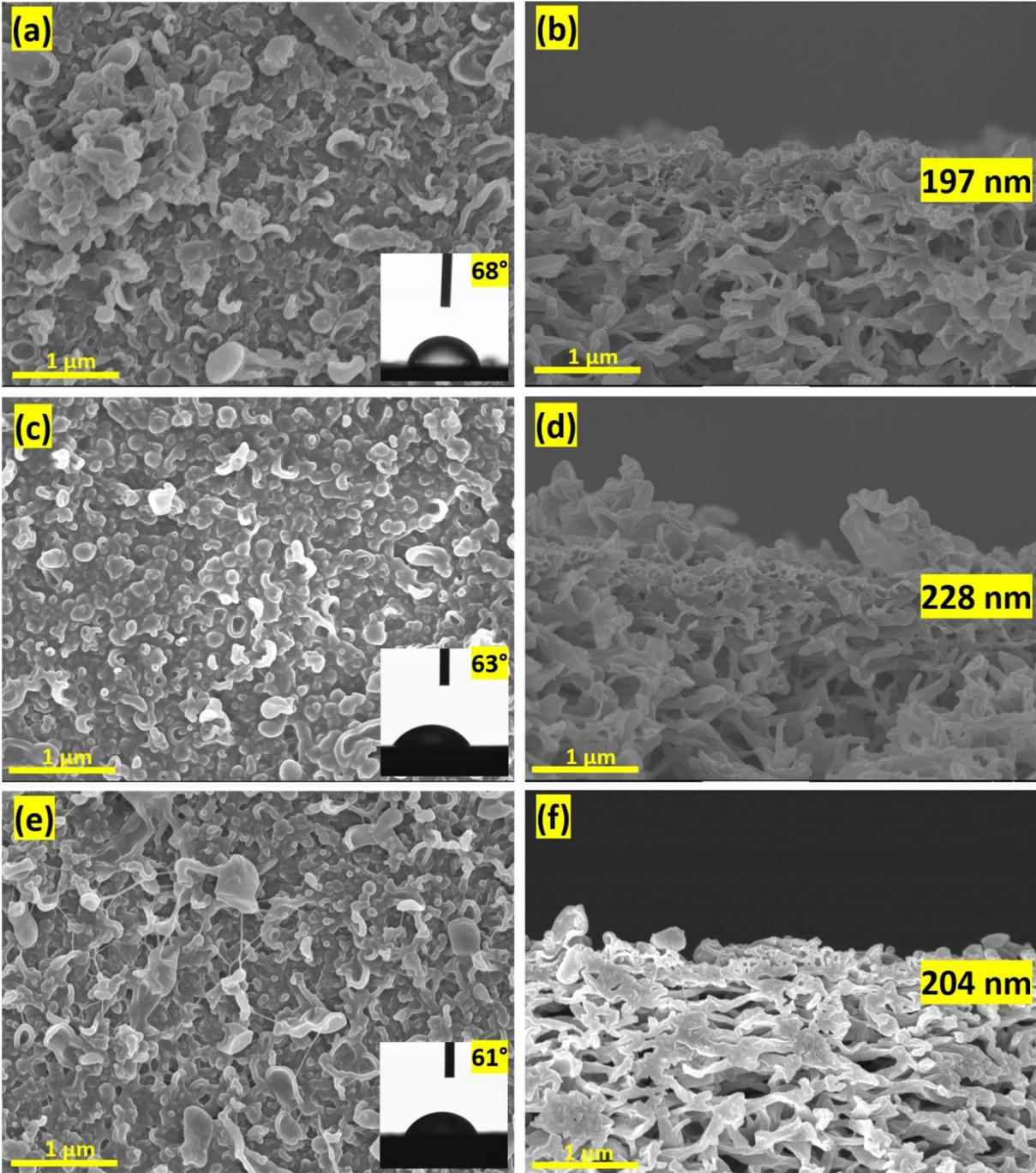
Figure 4. Surface and cross-section morphologies of the TFC membranes formed with the [a-b] pristine polyketone substrate (PK-TFC), and reduced polyketone substrates ([c-d] rPK-1-TFC and [e-f] rPK-2-TFC). TFC membrane surface water contact angle are indicated inset.

3.3. TFC membrane morphology

Figure 4 shows the membrane morphology of the TFC membranes prepared in this study. Characterization of the surface shows the successful formation of the polyamide active layer on the polyketone substrates, regardless of the reduction procedure. The ridge-and-valley structures characteristic of polyamide can be seen, and the cross-section images are used to measure the thickness of the active layer thin films of each membrane sample. The cross-section images show further the interconnected fibril-like structure of polyketone, indicating the high degree of porosity of polyketone. Finger-like porous structures were not visible from the FE-SEM images, while the quite denser sponge-like porous structures were visible towards the bottom surface of the membranes. The surface water contact angles of the three membranes shown in Figure 4 were similar.

3.4. Membrane intrinsic transport properties and osmotic performance

The intrinsic membrane transport properties of the TFC membranes are tabulated in **Table 1**. PK-TFC has an A value of 1.12 L m^{-2} h^{-1} bar^{-1}, while the most water-permeable membrane rPK-2-TFC has an A value of 1.92 L m^{-2} h^{-1} bar^{-1}. The formation of a stable polyamide active layer on the substrates was further suggested by the solute rejection capacity of the membranes. All three membranes have outstanding rejection of above 95%, and the solute permeability coefficient (B) were all significantly lower than A, that the B/A value of all three membranes were less than 0.15 bar.

315 **Table 1**. The intrinsic transport properties (water permeability coefficient, *A*, and solute

316 permeability coefficient, *B*) of the TFC membranes.

Membrane	A (L m^{-2} h^{-1} bar^{-1})	B (L m^{-2} h^{-1})	R (%)	B/A (bar)
PK-TFC	1.12 ± 0.13	0.14 ± 0.03	98.0	0.125
rPK-1-TFC	1.45 ± 0.08	0.17 ± 0.05	96.5	0.117
rPK-2-TFC	1.92 ± 0.21	0.28 ± 0.07	95.7	0.146

317

318 Osmotic performance was tested during FO operation of the membranes. Two sets of osmotic

319 performance studies were performed: (1) comparison of the AL-FS and AL-DS orientations using

320 DI water and 1.0 M NaOH as feed and draw, and (2) comparison of the water flux obtained as

321 different concentrations of NaCl were used as the draw. The osmotic performance of the

322 membranes is shown in **Figure 5**. Water flux values obtained at AL-DS orientation are found to

323 be higher than those obtained at AL-FS orientation, since the feed is facing the membrane substrate

324 during AL-DS orientation, thus there is less internal concentration polarization (ICP) [27]. The

325 best performing membrane was rPK-2-TFC, with J_w values of 34.7 and 37.8 L m^{-2} h^{-1}, for AL-FS

326 and AL-DS orientations, respectively. The J_w of rPK-1-TFC are 26.6 (AL-FS) and 28.0 (AL-DS)

327 L m^{-2} h^{-1}. These water flux values were significant enhancements from those of the control PK-

328 TFC membrane, whose water flux values for AL-FS and AL-DS orientations are 16.3 and 19.6 L

329 m^{-2} h^{-1}, respectively. Consistent with the solute permeability coefficient, the TFC membranes also

330 demonstrated outstanding selectivity, with low specific reverse salt flux values. As shown in

331 **Figure 5(c)**, operating FO with different concentrations of draw solution led to higher water flux

332 values as the concentration of draw increased. This is primarily due to the higher osmotic driving

333 force present at higher concentration difference of the draw and feed solutions.
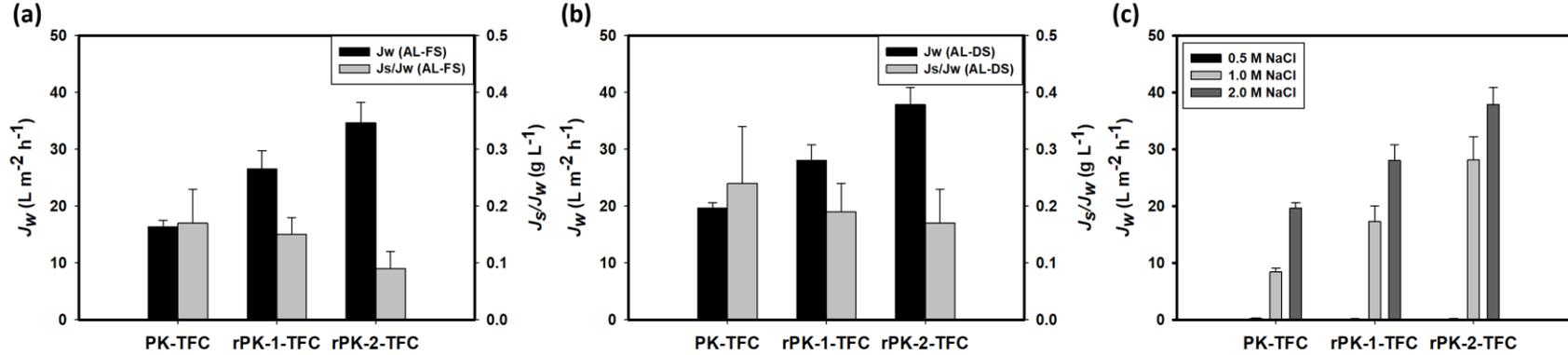
Figure 5. Osmotic performance of the TFC membranes during FO operation: (a-b) the water flux and specific reverse salt flux values for (a) AL-FS and (b) AL-DS mode with DI water and 1.0 M NaCl as feed and draw, respectively; and (c) the water flux values at AL-DS mode with DI water as feed and different concentrations of NaCl (0.5 – 2 M) as draw.

3.5. Membrane fouling

Membrane fouling was observed for the membranes using a variety of representative model foulants. Soybean oil, whose chemical formula is $C_{57}H_{98}O_{12}$, was chosen as the model oil foulant, due to its significantly high molecular weight and capacity to be adsorbed within the pores of the membrane. Representative protein (BSA), carbohydrate (sodium alginate), and humics (humic acid) foulants were also chosen to exhibit the anti-fouling propensity of the membranes. All soybean oil-in-water emulsions used in this study were stabilized using 0.01 ppm SDS surfactant.

During the osmotic performance with 1% (v/v) soybean oil-in-water emulsion as feed and 1.0 M NaCl as draw, the membranes were tested for FO for 8 h, and the average water flux, specific reverse salt flux, and oil flux values are tabulated in **Table 2**. Despite the presence of oil in the feed, there was no observed significant decrease compared with the water flux values obtained with DI water as feed. After 8 h operation, even the reverse salt flux remained satisfactory and comparable with those of the membranes operated with soybean oil-less feed solution. Oil flux values were also determined to see how effective the membranes are in rejecting oil. PK-TFC exhibited an oil flux value of 0.022 g m^{-2} h^{-1}, while the membranes prepared using the reduced polyketone substrate had significantly lower oil flux of 0.010 and 0.006 g m^{-2} h^{-1} for rPK-1-TFC and rPK-2-TFC, respectively, due to the higher substrate hydrophilicity.

The antifouling ability of the TFC membranes were put to test during FO operation with model foulants as the feed. Figure 6 shows the water flux profiles of the TFC membranes during FO operation at AL-DS mode for the different model foulants: 1% (v/v) soybean oil-in-water emulsion, and three different solutions of 1% (v/v) soybean oil mixed with 100 ppm each of BSA, sodium alginate, and humic acid. Fouling tests were conducted for a period of 8 h per membrane

360   per foulant solution. The flux values were normalized by division with initial values for better

361   understanding of how the flux was affected during the entire operation.

362   As expected, fouling significantly affected the control PK-TFC membrane. The oil-in-water

363   solution caused a flux decline of 18% after 8 h operation, while the mixture containing humic acid,

364   sodium alginate, and BSA marked flux declines of 26, 37, and 44%, respectively. The foulant

365   molecules entered the substrate porous structure, and the deposition onto the pores caused internal

366   fouling, which resulted to a heightened water transport resistance, thus sharp water flux declines

367   were observed.

368   The rPK-2-TFC membrane exhibited the best antifouling behavior among the three

369   membranes, with rPK-1-TFC not too far behind. Among the four foulant solutions, the soybean

370   oil-in-water emulsion and soybean oil-in-water emulsion mixed with humic acid showed

371   insignificant flux decline over the 8 h operation period, marking only 8 and 11% decrease in water

372   flux for the rPK-2-TFC membrane. With the foulant solutions mixed with sodium alginate and

373   BSA, there were more significant declines in water flux after FO operation of 8 h. 15% water flux

374   declines were observed with the oil-in-water emulsion feed solution spiked with sodium alginate

375   and BSA. Among the three membranes, rPK-1-TFC also showed highly satisfactory fouling

376   mitigation performance, as evidenced by its flux decline of 11, 15, 21, and 23% for the oil-in-water

377   emulsion, as well as the emulsions containing humic acid, sodium alginate, and BSA, respectively.

378   The low water flux decline marked with only oil-in-water emulsion feed solution is due to the

379   oleophobicity of the PK membrane substrate. The same oleophobic nature of the membrane

380   substrate worked as well for rejection of the humics substances, since this type of foulant is known

381   to be consisted of hydrophobic functional groups [28]. In the case of sodium alginate and BSA,

382   these two foulants are characterized by their larger molecular weights, and larger molecules are

383 known to cause more severe fouling. Larger molecules, such as polysaccharides (alginate) and

384 proteins (BSA), tend to aggregate more on the membrane pores and cause fouling, and can be

385 mitigated by the presence of negatively-charged surface [29]. Polyketone, when reduced, exhibits

386 an electroneutral surface [18], which may prove to be useful for oleophobicity, but not for

387 mitigation of fouling with negative foulants. Thus, even in the case of rPK-2-TFC, 15% water flux

388 decline was observed when the feed containing sodium alginate and BSA was used.

389   The self-cleaning ability of the membranes was evaluated after a simple backwash in

390 between the fouling performance tests. The pristine membrane exhibited a flux recovery of 67%

391 after backwashing. This indicates that while the pristine PK membrane is generally hydrophilic

392 and oleophobic, the oil and foulants adsorbed on the membranes are not easily washed out. In the

393 case of the membranes with reduced polyketone substrates, flux recovery was observed to be as

394 high as 89% and 95% for rPK-1-TFC and rPK-2-TFC, respectively. The self-cleaning ability

395 during wetting with water is among the known properties of highly hydrophilic membranes. The

396 added oleophobic characteristic of the reduced polyketone substrates further aids in the self-

397 cleaning process, as water can be adsorbed onto the pores despite being fully wetted by oil. These

398 results indicate that antifouling and self-cleaning membranes can be used for effective treatment

399 of problematic feed water, such as oily wastewater.

400

401 **Table 2**. Osmotic performance of the TFC membranes during FO operation using 1.0 M NaCl and

402 1 (v/v) soybean oil-in-water emulsion as the draw and feed, respectively.

Membrane	Water flux, J_w ($L\,m^{-2}\,h^{-1}$)	Specific reverse salt flux, J_s/J_w ($g\,L^{-1}$)	Oil flux, J_o ($g\,m^{-2}\,h^{-1}$)
PK-TFC	13.8 ± 1.27	0.36	0.022
rPK-1-TFC	25.8 ± 2.11	0.29	0.010
rPK-2-TFC	34.9 ± 2.86	0.32	0.006

403
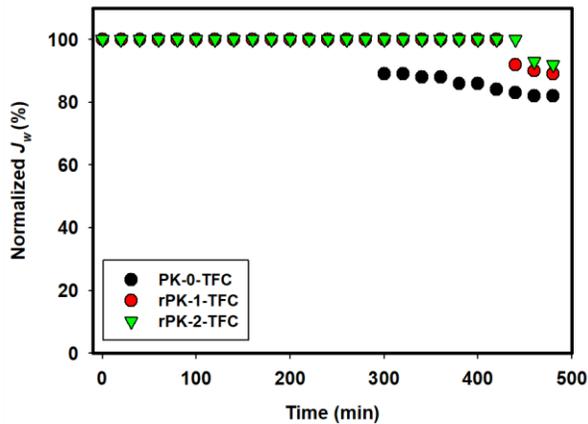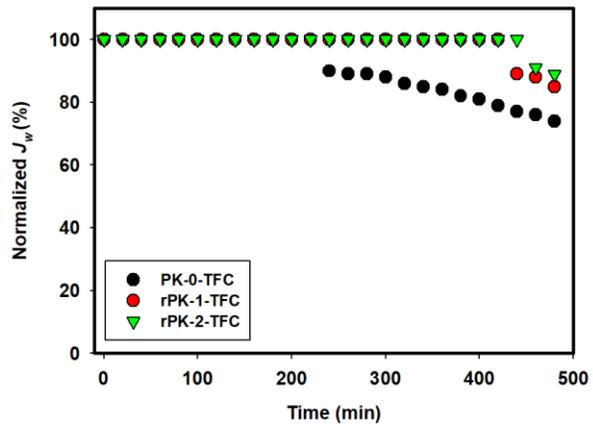
Figure 6. Water flux profiles of the TFC membranes during FO operation at AL-DS mode for the different model foulants: (a) 1% (v/v) soybean oil; (b) 1% (v/v) soybean oil and 100 ppm humic acid; (c) 1% (v/v) soybean oil and 100 ppm sodium alginate; and (d) 1% (v/v) soybean oil and 100 ppm bovine serum albumin. (Normalized flux values are the quotient of the flux and the initial flux readings).

410
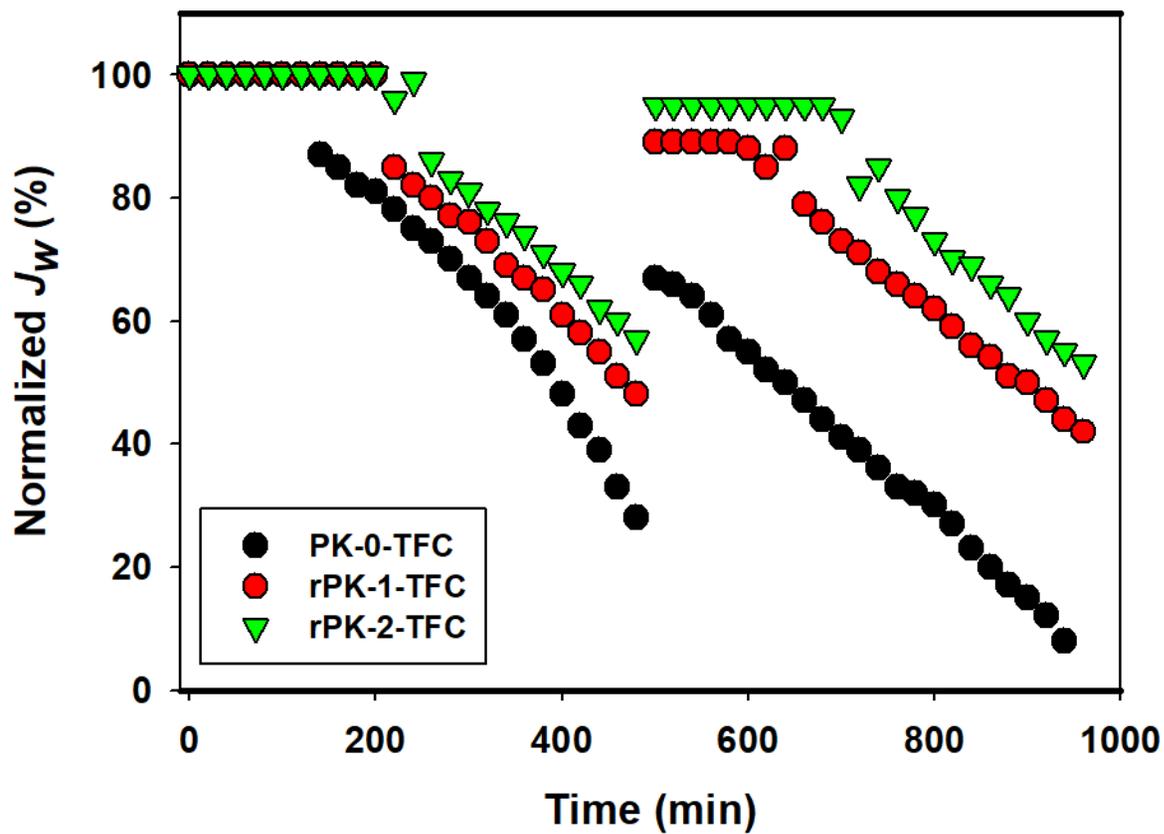
Figure 7. Water flux of PK-TFC, rPK-1-TFC, and rPK-2-TFC with the comprehensive fouling

solution (containing (1% (v/v) soybean oil and 100 ppm each of bovine serum albumin, sodium

alginate, and humic acid) over two 8 h cycle operations.

4. Conclusion

TFC membranes with reduced polyketone substrates were prepared using a facile method in this study. Due to the chemical modification process, the reduced PK substrates exhibited highly hydrophilic and oleophobic properties. As an effect of the membrane surface chemistry and the intrinsic highly porous structure of polyketone, the TFC membranes showed outstanding water flux and fouling resistance against a variety of model foulants, in comparison with the control polyketone membrane. The rPK TFC membranes also have shown highly satisfactory self-cleaning ability, as evidenced by high flux recovery ratios after simple backwashing. This study proves that a simple modification and preparation method of the substrate for the preparation of TFC membranes can be used for effective treatment of problematic oily wastewater.

References

[1] K. Lutchmiah, A.R.D. Verliefde, K. Roest, L.C. Rietveld, E.R. Cornelissen, Forward osmosis for application in wastewater treatment: A review, Water Research, 58 (2014) 179-197.

[2] J.E. Kim, S. Phuntsho, F. Lotfi, H.K. Shon, Investigation of pilot-scale 8040 FO membrane module under different operating conditions for brackish water desalination, Desalination and Water Treatment, 53 (2015) 2782-2791.

[3] F. Volpin, L. Chekli, S. Phuntsho, J. Cho, N. Ghaffour, J.S. Vrouwenvelder, H. Kyong Shon, Simultaneous phosphorous and nitrogen recovery from source-separated urine: A novel application for fertiliser drawn forward osmosis, Chemosphere, 203 (2018) 482-489.

[4] D.I. Kim, G. Gwak, M. Zhan, S. Hong, Sustainable dewatering of grapefruit juice through forward osmosis: Improving membrane performance, fouling control, and product quality, Journal of Membrane Science, 578 (2019) 53-60.

[5] R.R. Gonzales, M.J. Park, T.-H. Bae, Y. Yang, A. Abdel-Wahab, S. Phuntsho, H.K. Shon, Melamine-based covalent organic framework-incorporated thin film nanocomposite membrane for enhanced osmotic power generation, Desalination, 459 (2019) 10-19.

[6] F. Volpin, R.R. Gonzales, S. Lim, N. Pathak, S. Phuntsho, H.K. Shon, GreenPRO: A novel fertiliser-driven osmotic power generation process for fertigation, Desalination, 447 (2018) 158-166.

[7] W.J. Lee, P.S. Goh, W.J. Lau, C.S. Ong, A.F. Ismail, Antifouling zwitterion embedded forward osmosis thin film composite membrane for highly concentrated oily wastewater treatment, Separation and Purification Technology, 214 (2018) 40-50.

[8] D.I. Kim, R.R. Gonzales, P. Dorji, G. Gwak, S. Phuntsho, S. Hong, H. Shon, Efficient recovery of nitrate from municipal wastewater via MCDI using anion-exchange polymer coated electrode embedded with nitrate selective resin, Desalination, 484 (2020) 114425.

448 [9] X. Wu, M. Shaibani, S.J.D. Smith, K. Konstas, M.R. Hill, H. Wang, K. Zhang, Z. Xie, Microporous carbon
449 from fullerene impregnated porous aromatic frameworks for improving the desalination performance of
450 thin film composite forward osmosis membranes, Journal of Materials Chemistry A, 6 (2018) 11327-11336.
451 [10] R.R. Gonzales, Y. Yang, M.J. Park, T.-H. Bae, A. Abdel-Wahab, S. Phuntsho, H.K. Shon, Enhanced water
452 permeability and osmotic power generation with sulfonate-functionalized porous polymer-incorporated
453 thin film nanocomposite membranes, Desalination, 496 (2020) 114756-114765.
454 [11] M.J. Park, R.R. Gonzales, A. Abdel-Wahab, S. Phuntsho, H.K. Shon, Hydrophilic polyvinyl alcohol
455 coating on hydrophobic electrospun nanofiber membrane for high performance thin film composite
456 forward osmosis membrane, Desalination, 426 (2018) 50-59.
457 [12] Y. Wang, Z. Fang, C. Xie, S. Zhao, D. Ng, Z. Xie, Dopamine incorporated forward osmosis membranes
458 with high structural stability and chlorine resistance, Processes, 6 (2018) 151.
459 [13] R.R. Gonzales, M.J. Park, L. Tijing, D.S. Han, S. Phuntsho, H.K. Shon, Modification of nanofiber support
460 layer for thin film composite forward osmosis membranes via layer-by-layer polyelectrolyte deposition,
461 Membranes, 8 (2018) 70-84.
462 [14] Y. Li, S. Qi, Y. Wang, L. Setiawan, R. Wang, Modification of thin film composite hollow fiber
463 membranes for osmotic energy generation with low organic fouling tendency, Desalination, 424 (2017)
464 131-139.
465 [15] J. Wang, S. Zhang, P. Wu, W. Shi, Z. Wang, Y. Hu, In situ surface modification of thin-film composite
466 polyamide membrane with zwitterions for enhanced chlorine resistance and transport properties, ACS
467 Applied Materials & Interfaces, 11 (2019) 12043-12052.
468 [16] H.M. Hegab, A. ElMekawy, T.G. Barclay, A. Michelmore, L. Zou, C.P. Saint, M. Ginic-Markovic, Fine-
469 tuning the surface of forward osmosis membranes via grafting graphene oxide: Performance patterns and
470 biofouling propensity, ACS Applied Materials & Interfaces, 7 (2015) 18004-18016.
471 [17] S. Jafarinejad, H. Park, H. Mayton, S.L. Walker, S.C. Jiang, Concentrating ammonium in wastewater by
472 forward osmosis using a surface modified nanofiltration membrane, Environmental Science: Water
473 Research & Technology, 5 (2019) 246-255.
474 [18] L. Cheng, A.R. Shaikh, L.-F. Fang, S. Jeon, C.-J. Liu, L. Zhang, H.-C. Wu, D.-M. Wang, H. Matsuyama,
475 Fouling-resistant and self-cleaning aliphatic polyketone membrane for sustainable oil-water emulsion
476 separation, ACS Applied Materials & Interfaces, 10 (2018) 44880-44889.
477 [19] Y. Sun, L. Cheng, T. Shintani, Y. Tanaka, T. Takahashi, T. Itai, S. Wang, L. Fang, H. Matsuyama,
478 Development of high-flux and robust reinforced aliphatic polyketone thin-film composite membranes for
479 osmotic power generation: Role of reinforcing materials, Industrial & Engineering Chemistry Research, 57
480 (2018) 13528-13538.
481 [20] K. Nakagawa, K. Uchida, J.L.C. Wu, T. Shintani, T. Yoshioka, Y. Sasaki, L.-F. Fang, E. Kamio, H.K. Shon,
482 H. Matsuyama, Fabrication of porous polyketone forward osmosis membranes modified with aromatic
483 compounds: Improved pressure resistance and low structural parameter, Separation and Purification
484 Technology, 251 (2020) 117400.
485 [21] L. Zhang, Y. Lin, L. Cheng, Z. Yang, H. Matsuyama, A comprehensively fouling- and solvent-resistant
486 aliphatic polyketone membrane for high-flux filtration of difficult oil-in-water micro- and nanoemulsions,
487 Journal of Membrane Science, 582 (2019) 48-58.
488 [22] L. Zhang, Y. Lin, H. Wu, L. Cheng, Y. Sun, T. Yasui, Z. Yang, S. Wang, T. Yoshioka, H. Matsuyama, An
489 ultrathin in situ silicification layer developed by an electrostatic attraction force strategy for ultrahigh-
490 performance oil–water emulsion separation, Journal of Materials Chemistry A, 7 (2019) 24569-24582.
491 [23] O. Ohsawa, K.-H. Lee, B.-S. Kim, S. Lee, I.-S. Kim, Preparation and characterization of polyketone (PK)
492 fibrous membrane via electrospinning, Polymer, 51 (2010) 2007-2012.
493 [24] Q. Zhang, Z. Zhang, L. Dai, H. Wang, S. Li, S. Zhang, Novel insights into the interplay between support
494 and active layer in the thin film composite polyamide membranes, Journal of Membrane Science, 537
495 (2017) 372-383.

496 [25] S. Wang, K. Gu, J. Wang, Y. Zhou, C. Gao, Enhanced the swelling resistance of polyamide membranes
497 with reinforced concrete structure, Journal of Membrane Science, 575 (2019) 191-199.
498 [26] I.L. Alsvik, M.-B. Hägg, Preparation of thin film composite membranes with polyamide film on
499 hydrophilic supports, Journal of Membrane Science, 428 (2013) 225-231.
500 [27] G.T. Gray, J.R. McCutcheon, M. Elimelech, Internal concentration polarization in forward osmosis:
501 Role of membrane orientation, Desalination, 197 (2006) 1-8.
502 [28] Y.-F. Guan, B.-C. Huang, Y.-J. Wang, B. Gong, X. Lu, H.-Q. Yu, Modification of forward osmosis
503 membrane with naturally-available humic acid: Towards simultaneously improved filtration performance
504 and antifouling properties, Environment International, 131 (2019) 105045.
505 [29] Y. Liu, B. Mi, Combined fouling of forward osmosis membranes: Synergistic foulant interaction and
506 direct observation of fouling layer formation, Journal of Membrane Science, 407-408 (2012) 136-144.

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