Improvement of the swelling properties of ionic hydrogels by the incorporation of hydrophobic, elastic microfibers for forward osmosis applications

Ranwen Ou, Huacheng Zhang, Seungju Kim, George P. Simon, Hongjuan Hou and Huanting Wang*

New Horizons Research Centre, Department of Chemical Engineering, Monash University, Clayton, Victoria 3800, Australia
Email: huanting.wang@monash.edu

New Horizons Research Centre, Department of Materials Science and Engineering, Monash University, Clayton, Victoria 3800, Australia

Energy and Environment Research Institute, Baosteel Group Corporation, Shanghai, 201999, China

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Abstract

The swelling properties of hydrogels as draw agents have been identified as one of the key parameters in determining the performance of polymer hydrogel-driven forward osmosis process. We report here a new strategy to improve the swelling property of hydrogels by the introduction of structural inhomogeneity and compressive forces in an ionic hydrogel for the purpose of increasing forward osmosis water flux. This is achieved by incorporating a hydrophobic, elastic polyester (PET) hollow microfiber into an ionic hydrogel under a compressive force during the preparation of the composite hydrogel monolith. The forward osmosis water flux of the composite hydrogels increased with increasing the microfiber loading and compression pressure. The composite hydrogel with 50 wt. % PET microfiber loading and 18 kPa compression pressure demonstrated the highest flux. The water flux of poly (NIPAM-co-SA) – PET microfiber composite prepared under 18 kPa compression (PN5S5 – PET-0.5/0.5-18) and poly (sodium acrylate) – PET microfiber composite (PSA –
PET-0.5/0.5--18) reached 3.0 and 5.0 LMH in the first 10 min, respectively, when their swelling ratio is 4. The water flux of the composites was twice as high as the pure hydrogel. The composite hydrogels were also better at maintaining high water fluxes for a long period. The water flux of PSA-PET-0.5/0.5-18 decreased from 3.5 to 1.4 LMH after 24 h forward osmosis test. The combination of hydrophilic ionic hydrogel and hydrophobic PET microfiber resulted in an extended, porous structure within the hydrogel because of their different wettability, whilst an additional relaxation force was preserved in the composites because of the compression pressure applied during the preparation. Both of these worked together to enhance the FO water flux and maintain it for an extended long period.
1. Introduction

One of the most pervasive problems afflicting the world is water scarcity; by 2025, nearly two-thirds of the world’s population are projected to face water shortage. Tremendous efforts have been made to search for environmental and cost friendly solutions to this problem. Among many other technologies, forward osmosis (FO) desalination is gaining growing attention. Such a process shows great potential to lower the costs of production of fresh water from saline water because solar energy and other low-grade heat can be directly used. In the FO process, a semi-permeable membrane is used as the separation medium, and the osmotic pressure difference on two sides of membrane acts as the driving force. The draw agent possesses a higher osmotic pressure than the feed solution which determines the performance of the FO process apart from the FO membrane. A number of materials have been investigated as draw agent, including salts, polar solvents, saccharide solutions, hydrophilic nanoparticles, polyelectrolytes and hydrogels. Of the materials studied to date, the stimuli responsive hydrogel draw agent which was originally reported by our group, shows great potential in the forward osmosis application because of the easy recovery of water and easy regeneration.

The swelling property of hydrogels and the effective contact between FO membrane and hydrogel are key parameters for achieving high water flux. The degree of contact between the membrane and hydrogel can be enhanced by decreasing the hydrogel particle size, increasing the softness of hydrogel, or in situ preparation of hydrogel monolith on the FO membrane itself. The swelling properties of hydrogels include the swelling kinetics and pressure. The swelling kinetics determine the swelling pattern of solvent diffusion and polymer chain relaxation, while the swelling pressure reveals the driving force of the hydrogel in the FO process. A simple and useful empirical equation is used to describe the swelling kinetics, the so called power law.
\[
\frac{M_t}{M_\infty} = kt^n
\]

where \( M_t \) and \( M_\infty \) are the amount of water absorbed at time \( t \) and equilibrium, respectively. \( k \) is the characteristic constant of the water-polymer system, and \( n \) is the characteristic exponent of the transport mode. The characteristic exponent \( n \) reveals whether the swelling process is a solvent diffusion controlled or polymer chain relaxation controlled process. The swelling pressure of polymer hydrogel originates from polymer-water mixing, elastic reaction force of the network, and the osmotic pressure of ionizable groups. The swelling pressure (\( \Pi \)) of an ionic gel can be expressed as the sum of three contributions from each component \(^{12-14}\):

\[
\Pi = \Pi_{\text{mix}} + \Pi_{\text{el}} + \Pi_{\text{ion}}
\]

where \( \Pi_{\text{mix}} \), \( \Pi_{\text{el}} \), and \( \Pi_{\text{ion}} \) are the mixing, elastic, and ionic contributions, respectively.

The swelling behavior of the hydrogel is strongly dependent on the crosslinking density, and the interactions between the solvent molecules and the polymeric chain segments \(^{12}\). Note that the swelling property of hydrogel can be modified by changing the crosslinking density \(^{15}\), introduction of ionic group \(^{8}\) and structural inhomogeneity \(^{16-18}\) and so on. Firstly, the crosslinking density plays a major role in determining the absorption properties of hydrogel. The water molecules cannot be held in a polymer network with a low crosslinking density, while a highly crosslinked polymer network does not allow the entrance of water. Secondly, the introduction of ionic groups is good for polymer-water mixing and the mixing of ions with solvent, and thus the configurational change of gel structure. Consequently, the solvent diffusion rate and the polymer chain relaxation rate are enhanced accordingly. Thirdly, introducing structural inhomogeneity such as hydrophilic tunnel or porosity accelerates the water diffusion in the hydrogel, which improves the polymer-water mixing, and thus enhances the solvent diffusion rate. In addition, a capillary force can be harnessed if
microscale, connected pores can be generated in the hydrogel, and can act as an additional driving force to accelerate the solvent diffusion.

In this paper, the swelling properties of hydrogels are modified by the introduction of structural inhomogeneity and compressive forces in the hydrogel. The structural inhomogeneity is introduced by addition of a hydrophobic microfiber (made of polyester) into an ionic hydrogel. The combination of hydrophobic, elastic polyester (PET) microfiber and hydrophilic hydrogel generates a porous structure, which is expected to be favorable for water transport. In this study, N-isopropyl acrylamide (NIPAM) and sodium acrylate (SA) were selected for preparing the hydrophilic hydrogel; NIPAM offers the hydrogel thermal responsive ability, and SA endows the hydrogel higher ionic strength. In the preparation process, the mixture of PET microfiber and monomer solution is compressed during polymerization, so that part of the compression force due to the deformed fibres can be stored in the composite. We hypothesize that the addition of PET microfibers in hydrogel changes the swelling pattern from polymer chain relaxation controlled process to solvent diffusion controlled process, allowing it to attain a swelling equilibrium much more rapidly. In addition, because of elasticity of PET microfiber, the compressive force is released during the hydrogel swelling, enhancing polymer chain relaxation. The actual effects of the addition of PET microfibers and the introduction of compressive forces on the swelling pressure of the polymer hydrogel and the forward osmosis water flux are studied in detail.

2. Experimental

Materials

N-isopropyl acrylamide (NIPAM, 97 %%), Sodium acrylate (SA, 97 %), N, N-methylenebis (acrylamide) (MBA, 99 %), ammonium persulfate (APS, ≥ 98 %), and N, N, N’, N’-
tetramethyl ethylenediamine (TEMED, 99 %) were purchased from Sigma-Aldrich Australia, and used without further treatment. The polyester (PET) microfiber was the filler of Biozone Polyester Pillow (High & Firm, Biozone). The PET microfiber was washed with ethanol (99.7 %, Merck) and pure water for 3 times, followed by drying in a 45 °C oven before use. The average diameter of the PET microfiber was about 34 μm, which was determined by analyzing the SEM images using Nano Measurer 1.2. Pure water was used in all experiments.

Preparation of pure ionic hydrogel: Monomer (NIPAM, SA), crosslinker (MBA), and initiator (APS) were dissolved in pure water to form a 16.67 wt. % monomer solution. The weight ratio of NIPAM, SA, MBA, and APS was fixed at 25:25:1:0.5. The ionic hydrogel contained 50 wt. % NIPAM and 50 wt. % SA (PN5S5). In order to get better contact between hydrogel and membrane, a monolithic sample was used in this study. 3 g of monomer solution containing 0.5 g of monomer was transferred into a FO cell after deaeration via flowing N₂ gas through the solution for 10 min, and a drop of TEMED was then added into the solution under mild shaking to accelerate the polymerization. The monolithic hydrogel was formed on the FO membrane (CTA membrane, Hydration Technologies Inc., Albany, OR) in a few minutes, followed by rinsing with pure water 3 times.

Preparation of composite hydrogels: 3 g of monomer solution after deaeration was added into a FO cell, and a drop of TEMED was added as above. Then, a given amount of PET microfiber was added to the solution, followed by pressing the fiber and solution with weight, as shown in Fig. S1 (Supporting Information). The amount of the PET microfiber and the compression pressure applied in the polymerization process are shown in Table 1. A polydopamine-coated PET (D-PET) microfiber was also prepared. The hydrogel-D-PET composite was compared with hydrophobic microfiber – hydrogel composite in terms of their microstructure and FO performance. The hydrogel-D-PET composite was prepared using the same procedure described above.
<table>
<thead>
<tr>
<th>Hydrogel</th>
<th>NIPAM+SA /g</th>
<th>PET microfiber /g</th>
<th>Compression pressure /kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>PN5S5</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PN5S5-PET-0.5/0.15</td>
<td>0.5</td>
<td>0.15</td>
<td>18</td>
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<tr>
<td>PN5S5-PET-0.5/0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0, 8, 18</td>
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<tr>
<td>PN5S5-PET-0.5/1.0</td>
<td>0.5</td>
<td>1.0</td>
<td>18</td>
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</table>

**Characterization:** The morphology of the pure hydrogel and hydrogel-PET composites was probed using a scanning electron microscope (Nova NanoSEM 450 FESEM, FEI, USA). The wettability of PET microfiber and hydrogels was determined by a contact angle goniometer (Dataphysics OCA15, Dataphysics, Germany). An industrial incandescent lamp (IR 250C, 230 V, 250 W, Philips) was used as light / heat source for dewatering the swollen hydrogel draw agent, and a radiometer (FZ-A) was applied to determine the light intensity. A true-rms digital multimeter (38 XR-A, Amprobe, USA) measured the temperature change of hydrogel during the dewatering.

A gravimetric method was utilized to investigate the swelling behaviors of hydrogels with different PET microfiber loading and compression pressure. A dry monolith hydrogel was put into 2 L of pure water. The weight of swollen hydrogels was weighed until it reaches an equilibrium. The swelling ratio (Q) of hydrogels as a function of time was calculated as follows:

$$Q(t) = \frac{w_t - w_d}{w_d}$$  \hspace{1cm} (3)

where $w_t$ (g) is the weight of swollen hydrogel at time $t$ and $w_d$ (g) is the weight of dry hydrogel before the test.

The forward osmosis water flux was determined in a home-made FO cell (Fig. S1, Supporting Information). In the FO mode, the active surface of the FO membrane faced the
feed solution, while the hydrogel monolith was prepared on the bottom surface. The monolith contained 0.5 g of hydrogel with different amounts of water, while the composites had different amounts of PET microfiber. The initial swelling ratio of the hydrogel was calculated based on the 0.5 g hydrogel in each monolith. 2000 ppm NaCl solution was used as the feed solution for all measurements. FO water flux, \( F (L \cdot m^{-2} \cdot h^{-1} \), or LMH) were determined by the weight change of FO cell with hydrogel over a period of time, as follows:

\[
F = \frac{V}{A \times t}
\] (4)

where \( V \) (L) is the volume change of hydrogel over a period of time \( t \) (h). The effective area \( A \) (m\(^2\)) of the FO membrane is 4.91 cm\(^2\).

The swelling pressure of hydrogel was roughly estimated according to the method described elsewhere \(^3\). The hydrogel (swelling ratio = 5) was placed on the active side of a FO membrane in the FO cell, and NaCl solution (2, 20, 50, 100, and 200 g/L) was put on the other side of the membrane. The hydrogel was allowed to absorb water for 24 h at room temperature to reach equilibrium. The initial swelling ratio of the hydrogel was 5 because it was relatively soft and had good contact with the FO membrane. The final swelling ratio of the hydrogel at a given NaCl concentration may be different from the initial swelling ratio, the hydrogel may absorb or desorb water to reach equilibrium.

In the dewatering process, the swollen hydrogel monolith was put under an incandescent lamp with a light intensity of 1 kW·m\(^2\), the weight loss of the hydrogel as a function of time was recorded. The average dewatering flux was calculated according to Equation (4). In order to recover the liquid water released during the solar dewatering, a setup in Fig. S2 (Supporting Information) was used. The swollen hydrogel was put on a microfiltration membrane (Sterlitech, 100 nm pore size) above the funnel. The microfiltration membrane was used to separate the hydrogel from water recovered. When liquid water was observed on the
membrane during the dewatering process, it was collected by turning on a vacuum pump (140 mL piston syringe pump, Monoject TM) for a few seconds. The liquid water recovery ($R_l$, %) was calculated as follows:

$$R_l = \frac{w_l}{w} \times 100$$

where $w_l$ (g) is the weight of liquid water recovered, and $w$ (g) is the total water recovered, including vapor and liquid.

3. Results and Discussion

3.1. Microstructure of composites

The SEM image of PN5S5 hydrogel (Fig. S3a, Supporting Information) shows that the dry monolith hydrogel has a dense and continuous polymer network structure. Fig. S3b (Supporting Information) demonstrates that the PET microfiber is hollow. The surface and cross-sectional morphology of composite hydrogels are shown in Fig. 1. The addition of PET microfibers into NIPAM-SA hydrogel endows the composite with pores, and the composite become more porous with increasing amount of PET microfiber, as observed in Fig. 1d, e, f. The formation of the porous structure can be explained by the distinct wettability of ionic hydrogel and PET microfibers. The hydrophobic PET microfibers are partially wetted by the monomer solution initially, and then the pores result produced after the polymerization.

3.2. Swelling properties of hydrogel

The effect of PET microfiber loading and compression pressure on the swelling properties of hydrogel was studied, as shown in Fig. 2 and Fig. 3. In general, a swelling process involves the diffusion of a solvent into a polymer, with the polymer chains changing their conformation to form a rubbery (swollen) polymer material. The equilibrium swelling ratio of PN5S5 and PN5S5-PET-0.5/0.5-18 are 64 and 37 g/g, respectively. The equilibrium swelling
ratio of PN5S5-PET-0.5/0.5-18 is about half of PN5S5, because it contains 50 wt. % of PET microfiber that does not swell in water. As shown in Fig. 2a, the sigmodal swelling curves implied three distinct stages of swelling: the movement of swelling front until meeting at the rigid core, the acceleration of swelling kinetics, and reaching of equilibrium swelling \(^9,20\). In the first stage, when a hydrogel in its initial state is in contact with solvent (water), the water penetrates into the polymeric network. Thus, the unsolvated glassy phase of the hydrogel is separated from rubbery hydrogel region with a moving boundary. The unsolvated glassy core in the middle of the hydrogel is the “rigid core”. The initial parts of the sigmodal curves of PN5S5 and its composite were distinctly different, owing to the difference of microstructure. Pure PN5S5 hydrogel was dense and continuous, while the hydrogel-PET composite showed porous structure. The porous structure caused a rapid water uptake, causing the composites to reach a much higher swelling ratio compared to PN5S5, in first 0.5 h. At 0.5 h, PN5S5-PET-0.5/0.5-18 showed higher swelling ratio than PN5S5-PET-0.5/1.0-18, possibly due to the fact that the higher concentrations of hydrophobic PET microfibers may hinder water transport. On the other hand, water was able to reach the core of PN5S5 hydrogel by diffusion in the polymer network and through the pores. The hydrophobic microfiber and pores led to the formation of a disconnected polymer hydrogel network, and decreased hydrogel size. Thus, the advancing swollen front in the composite hydrogel reached the rigid core much more rapidly than the large pure hydrogel monolith, being in the second stage of swelling; the network relaxation rate becoming greater than the rate of solvent diffusion. The acceleration of swelling kinetics of composite hydrogel occurred earlier at 1\(^{\text{st}}\) h, while that of PN5S5 hydrogel alone occurred after 2.5 h of swelling. PN5S5, PN5S5-PET-0.5/0.5-18, and PN5S5-PET-0.5/1.0-18 took 24, 6.5, and 11 h to reach equilibrium, respectively.
Fig. 1. (a-c) Surface and (d-f) cross-sectional SEM images of composite hydrogels. (a, d) PN5S5-PET-0.5/0.15, (b, e) PN5S5-PET-0.5/0.5, (c, f) PN5S5-PET-0.5/1.0. The compressive pressure applied is 18 kPa.
Fig. 2. (a) Swelling ratio and (b) swelling kinetics of hydrogels with different loadings of PET microfibers, and (c) forward osmosis water flux induced by the hydrogel and its composites. The unit of t on the x-axis of (a) and (b) is h. The initial swelling ratio of hydrogels was 4 for the FO water flux test. The composites used in this measurement were prepared under 18 kPa pressure.

The relation between solvent diffusion rate and polymer chain relaxation rate distinguishes the swelling pattern of the hydrogel. The simplest equation describing the swelling of a polymer is the power law (Equation (1)), where n is the characteristic exponent of the
transport mode. For a slab sample, n=0.5 indicates Fickian diffusion, n=1.0 indicates Case II transport, while 0.5<n<1.0 implies anomalous transport. Fickian diffusion is a solvent diffusion-controlled process, whilst Case II transport is a polymer chain relaxation controlled process. However, when the water penetration rate is much smaller than the polymer chain relaxation rate, it is possible to achieve n values less than 0.5, which is still regarded as Fickian diffusion, named as “Less Fickian” behavior. As shown in Fig. 2b, n=0.87 means that the swelling of PN5S5 in water is mainly controlled by the polymer chain relaxation. After blending with PET microfiber, the values of n for PN5S5-PET-0.5/0.5-18 and PN5S5-PET-0.5/1.0-18 decrease to 0.45 and 0.35, respectively. These n values are lower than 0.5, which means that the swelling of composite hydrogels exhibit Less Fickian diffusion, and that the polymer chain relaxation rate is much faster than the solvent diffusion rate. This is caused by the porous structure of composite and the decreased hydrogel size, and thus the acceleration of swelling kinetics. Fig. 2c shows the forward osmosis water flux of hydrogels, the composite hydrogel showed higher water flux than the pure one, while PN5S5-PET-0.5/0.5-18 performed best, which was about twice as high as that of PN5S5. The FO water flux of hydrogels is well consistent with the swelling kinetics.

As shown in Fig. S4 (Supporting Information), the strips of PN5S5 and PN5S5-PET-0.5/0.5 were put vertically on rhodamine B aqueous solution to observe the swelling process. After 2 min, the height of RhB solution in the composite was 6.5 times as high as that of PN5S5. This confirms that the porous structure generated by addition of PET microfiber provides an extra driving force for the water absorption.
Fig. 3. (a) Swelling ratio and (b) swelling kinetics of PN5S5-PET-0.5/0.5 hydrogels prepared with different compression pressure, and (c) forward osmosis water flux induced by the hydrogel draw agent. The unit of t on the x-axis of (a) and (b) is h. The initial swelling ratio of hydrogels was 4 for the FO water flux test.

Fig. 3 shows the effect of compression pressure on the swelling kinetics and FO water flux. In this study, 0, 8, and 18 kPa were applied during the preparation of PN5S5-PET-0.5/0.5. The values of n in the composites prepared at 0, 8, and 18 kPa were 0.45, 0.39, and 0.35,
respectively, which decreases with greater compression pressure applied. The composites prepared under different compression pressure all exhibit Less Fickian diffusion. With greater compression pressure, the composites become more compact and denser, thus the relaxation force generated by the compressed microfiber is higher, which drives the composite swelling faster. The FO water flux generated by the composites prepared at 8 and 18 kPa is higher than that of with no pressure applied, which is consistent with the swelling kinetics. PSA hydrogel and the PSA-PET composite were also prepared and tested as draw agents; the FO water flux of PSA composite decreased with decreasing PET microfiber loading, and increased with increasing compression pressure. This result is similar to the PN5S5 one, as shown in Fig. S5 (Supporting Information). The highest water flux of PSA-PET-0.5/1.0-18 reached 5.0 LMH in the first 10 min, decreasing slowly to 4.3 LMH after 1 h of testing.

![Swelling ratio of PN5S5 and PN5S5-PET-0.5/0.5-18](image)

**Fig. 4.** Plot of swelling ratio of PN5S5 and PN5S5-PET-0.5/0.5-18 as a function of osmotic pressure of NaCl solution at equilibrium.

Fig. 4 shows the swelling ratio of pure hydrogel PN5S5 and the composite hydrogel PN5S5-PET-0.5/0.5-18 at different osmotic pressures. The swelling ratio of the composite hydrogel is higher than the pure hydrogel at different osmotic pressures. In other words, to reach the
same swelling ratio, a greater osmotic pressure of NaCl solution is required. For instance, when the swelling ratio is 5, 4.6 MPa and 10.1 MPa of osmotic pressure are needed for the pure hydrogel and the composite hydrogel with 50 wt. % PET microfiber and 18 kPa compression pressure, respectively. The increase in the required osmotic pressure may be explained as follows: (1) part of the compression pressure existing in the composite hydrogel acted as a driving force; (2) the microscale, porous structure endowed the composite with capillary forces, which also becomes part of the swelling pressure. Note that the dewatering of composite hydrogel with a small swelling ratio (e.g., < 5) becomes more difficult because of poor contact between the shrunk hydrogel and the membrane surface, and residual water on the membrane surface. This leads to a higher osmotic pressure of NaCl required for a small swelling ratio, but such an osmotic pressure may be greater than the actual swelling pressure of the hydrogel. Nevertheless, Fig. 4 provides a good basis for comparison of the pure hydrogel with the composite hydrogel. The decreasing trend of swelling ratio – osmotic pressure curve of PN5S5-PET is different from that of PN5S5, and the former decreased slower and showed relatively high swelling ratio in NaCl solution with a higher osmotic pressure. This indicated that the compression pressure and capillary forces that existed in the composite hydrogel were gradually reduced with the swelling of hydrogel, which helped sustain the high water flux for a longer period of time.
**Fig. 5.** Wettability of PET microfiber, polydopamine coated PET microfiber and their composite hydrogels. Water contact angle of (a) PET microfiber and (b) PN5S5-PET-0.5/0.5-18, (c) D-PET microfiber and (d) PN5S5-D-PET-0.5/0.5-18.

In our previous study, the addition of a hydrophilic Thermoplastic polyurethane (TPU) microfiber introduced channels around the fibers into composite hydrogels, which facilitated water transport. In this study, to further investigate how the surface wettability of the microfiber affects the properties and performance of composite hydrogel, PET microfibers were coated with polydopamine to modify their surface properties. Polydopamine is selected because it can be easily deposited on virtually all types of inorganic and organic substrates, and can form a hydrophilic coating firmly adhering to the bulk materials under mild polymerization conditions. The resulting polydopamine-coated PET microfibers are denoted as D-PET. Hydrogel composites incorporated with the same amounts of D-PET were prepared and compared with those hydrogel composites prepared with unmodified PET microfibers. Fig. S6 (Supporting Information) shows the SEM images of surface of PET and D-PET microfibers. The fiber surface became rougher after being coated with polydopamine, while the contact angle decreases from 151.2° to 127.5°, as shown in Fig. 5a & 5c. Even though the D-PET microfiber is still hydrophobic, NIPAM solution can spread into the microfibers in 3 s (Fig. S7b), while the contact angle of PET microfibers containing NIPAM solution is 132.3°. After incorporating these microfibers into composite hydrogels, the water droplets are instantly absorbed by PN5S5-PET; however in the case of PN5S5-D-PET, they initially spread on the surface, and are subsequently absorbed by the composite, as shown in Fig. 5 and Fig. S8 (Supporting Information). For the PN5S5-PET composite, the hydrophobic PET microfiber penetrates throughout the hydrogel monolith, thereby resulting in a porous structure. The D-PET microfiber was more compatible with the hydrogel, and the resulting D-PET/polymer hydrogel monolith showed a similar microstructure observed in our TPU-
hydrogel monolith in our previous study. It was reported that a hydrogel with many micron to millimetre scale pores could absorb a considerable amount of water in a very short period to fill the whole space.

The forward osmosis and dewatering performance of PN5S5-PET-0.5/0.5-18 and PN5S5-D-PET-0.5/0.5-18 were studied, and the result is shown in Fig. 6. When the swelling ratio of composite was 4, the water flux of PN5S5-PET-0.5/0.5-18 decreased from 3.0 to 2.4 LMH in 60 mins of testing, while that of PN5S5-D-PET-0.5/0.5-18 decreased from 3.5 to 2.0 LMH. When the swelling ratio of composites decreased to 0, the water flux result showed a similar trend. This demonstrated that the compact structure (PN5S5-D-PET) is good for higher initial water flux; whereas the porous structure (PN5S5-PET) is beneficial to maintaining a higher flux level for a longer period. This can be observed in the swelling ratio – osmotic pressure curves in Fig. 4.

As for the dewatering performance, the average dewatering flux of PN5S5-D-PET-0.5/0.5-18 was twice as high as that of PN5S5-PET-0.5/0.5-18, and the liquid water recovery of PN5S5-D-PET-0.5/0.5-18 was 3 times greater compared with PN5S5-PET-0.5/0.5-18. An explanation for this is that the channels around polydopamine-modified microfibers more favorably transported water out of the monolith during the dewatering, which increased the dewatering flux and the liquid water recovery.
Fig. 6. (a) Forward osmosis water flux and (b) dewatering performance of PN5S5-PET-0.5/0.5-18 and PN5S5-D-PET-0.5/0.5-18.

The 24 h water flux of PN5S5, PSA, and their PET microfiber composite was also measured. As shown in Fig. 7a, generally, the composite hydrogel showed a higher water flux than the pure hydrogels, whilst PSA-PET-0.5/0.5-18 performed better than PN5S5-PET-0.5/0.5-18. The water flux of PN5S5-PET-0.5/0.5-18 was 2.4 LMH for the initial 0.5 h, and then decreased to 0.94 LMH after 24 h. In contrast, the water flux of PN5S5 was 2.1 and 0.70 LMH at 0.5 and 24 h, respectively. The water flux of PSA-PET-0.5/0.5-18 decreased from 3.5 to 1.4 LMH in 24 h measurement, which demonstrated that this hydrogel – hydrophobic microfiber composite was able to maintain a relatively high flux over a long period. Fig. 7b shows the dewatering performance of hydrogels. The composite hydrogels exhibited lower average dewatering fluxes than hydrogel alone. The dewatering flux of PN5S5-PET-0.5/0.5-18 and PSA-PET-0.5/0.5-18 were about half of that of PN5S5 and PSA, respectively. In addition, the low thermal conductivity of PET (0.2 W m$^{-1}$ K$^{-1}$) likely reduced the rate of heat transfer. Fig. S9 in the Supporting Information demonstrated that the temperature of PN5S5-PET-0.5/0.5-18 and PSA-PET-0.5/0.5-18 increased more slowly than the relevant pure hydrogel. However, the liquid water recovery from composite hydrogels is twice as much as those of the corresponding pure hydrogel. That may be caused by the lower temperature of hydrogel during dewatering, which decreased the evaporating rate of recovered liquid water. Furthermore, the PET composite hydrogel showed good cycling performance as a draw agent in the FO process, as shown in Fig. S10 (Supporting Information). For the 3 cycles, the water flux decreased from 2.1 – 2.2 to 1.4 – 1.5 LMH in 3 h.
Fig. 7. (a) 24 hours FO water flux, and (b) dewatering performance of hydrogels. PN5S5-PET-0.5/0.5-18 and PSA-PET-0.5/0.5-18 were used in this test. The initial swelling ratio of the hydrogels is 2 based on the amount of hydrogel.

4. Conclusion

The swelling properties of an ionic hydrogel-polyester microfiber composite prepared whilst compressing the fibre web during synthesis has been studied in an effort to provide an additional mechanism to improve the properties of hydrogels as a forward osmosis draw agent. The combination of a hydrophilic ionic hydrogel and a hydrophobic PET microfiber mesh imparted to the composite hydrogel porosity, due to the different wettabilities, whilst at the same time providing an additional relaxation force during swelling because of the compression pressure applied to the web during the preparation. The characteristic exponent n of the composites decreased with increasing PET microfiber loading and increasing amount of compression. The hydrogel-PET composites exhibited less Fickian diffusion, indicating that the polymer chain relaxation rate is much faster than the solvent diffusion rate. On the other hand, the porous structure and the PET microfiber decreased the sizes of hydrogel domains, increasing solvent diffusion; the swelling equilibrium of PN5S5-PET-0.5/0.5-18 and PN5S5-PET-0.5/1.0-18 being reached after 6.5, and 11 h, which is much faster than that of PN5S5 (24 hours). With regards the forward osmosis application, the water flux of
hydrogels was consistent with the swelling kinetics result, i.e., it increased with increasing PET microfiber loading and increasing compression pressure. The highest water flux of PN5S5-PET-0.5/0.5-18 reached 3.0 LMH in the first 10 min, while that of PSA-PET-0.5/0.5-18 was 5.0 LMH. Compared to the composite prepared with a polydopamine-modified microfiber (PN5S5-D-PET), PN5S5-PET was better at maintaining higher water flux in a long period test. The water flux of PSA-PET-0.5/0.5-18 decreased from 3.5 to 1.4 LMH in a 24 h measurement.

The dewatering flux of PN5S5-PET-0.5/0.5-18 was not as rapid as PN5S5, because of the low thermal conductivity of PET (0.2 W m\(^{-1}\) K\(^{-1}\)) (since the hydrogel is made hydrophobic by application of heat, and thus the rate of its transmission is important). However, the liquid water recovery of composite was twice that of the pure hydrogel. This work demonstrates that the performance of forward osmosis hydrogel draw agent is closely related to the swelling properties of hydrogel, and the draw agent performance can be effectively improved by tailoring its swelling properties.

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**Supporting Information**

Preparation scheme, dewatering setup, SEM and optical image, FO water flux of PSA and PSA-PET, contact angle of PET and D-PET, temperature change of hydrogels during dewatering.
5. References


PET microfiber-hydrogel composite draw agent

Compression force stored

Swelling

Compression force being released

Water
Supporting Information

Improvement of the swelling properties of ionic hydrogels by the incorporation of hydrophobic, elastic microfibers for forward osmosis applications

*Ranwen Ou, Huacheng Zhang, Seungju Kim, George P. Simon, Hongjuan Hou and Huanting Wang*

R. Ou, Dr. H. C. Zhang, Dr S. Kim, Prof. H. T. Wang
New Horizons Research Centre, Department of Chemical Engineering, Monash University, Clayton, Victoria 3800, Australia
Email: huanting.wang@monash.edu

Prof. G. P. Simon
New Horizons Research Centre, Department of Materials Engineering, Monash University, Clayton, Victoria 3800, Australia

Dr Hongjun Hou
Energy and Environment Research Institute, Baosteel Group Corporation, Shanghai, 201999, China
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Fig. S1. The preparation process of hydrogel-PET microfiber composite. The composition and compression pressure loading of composite hydrogel is shown in Table 1 in the manuscript.

Fig. S2. The solar dewatering setup for measuring the liquid water recovery. A microfiltration membrane (Sterlitech, 100 nm pore size) is applied to block the hydrogel from water recovered. Vacuum is applied few times when liquid water can be found on membrane during the dewatering process. A 140 mL piston syringe (Monoject™) is used to produce a vacuum inside the filtering flask in order to drive the liquid water into this receptacle.
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Fig. S4. The optical images of pure PN5S5 hydrogel and PN5S5-PET-0.5/0.5 composite hydrogel (a) before and (b) after swelling in aqueous rhodamine B (RhB) solution. The image (b) was taken after 2 mins of absorption.

Fig. S5. The 60 mins forward osmosis water flux of PSA composite with (a) different PET fibers loading, and (b) different compressed pressure loading.
Fig. S6. SEM images of (a) PET microfiber and (b) polydopamine coated PET microfiber.

Fig. S7. Contact angle of PET (a, c) and D-PET (b, d) microfibers with NIPAM solution (a, b) and SA solution (c, d) as testing medium.
Fig. S8. Optical images of (a, b) PN5S5-PET and (c, d) PN5S5-D-PET hydrogel before and after dropping a drop of 100 ppm RhB solution.

Fig. S9. The temperature change of pure hydrogel and composite hydrogel during 60 mins solar dewatering under 1 kW/m² incandescent lamp: (a) PN5S5 and PN5S5-PET, (b) PSA and PSA-PET. PN5S5-PET-0.5/0.5-18 and PSA-PET-0.5/0.5-18 were used in this test.
**Fig. S10.** The cycle performance of PN5S5-PET-0.5/0.5-18 composite. Three hours water flux was measured in each cycle. 2000 ppm NaCl solution was used as feed.