Enhancement of anti-fouling properties and filtration performance of poly(ethersulfone) ultrafiltration membranes by incorporation of nanoporous titania nanoparticles

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Nanoporous titania nanoparticles (NTNs) were synthesized and used as an additive at a low concentration of 0.1 to 1 wt% in the fabrication of poly(ethersulfone) (PES) ultrafiltration membranes via non-solvent induced phase separation. The structure and properties of nanoparticles were characterized using nitrogen sorption, X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The NTNs have a size distribution with particle size mainly less than 100 nm and have a BET surface area of about 100 m² g⁻¹. The modified membranes were fabricated and investigated in terms of their pure water flux, solute rejection, and fouling resistance. The water permeability and molecular weight cut-offs (MWCO) of membranes were determined under constant pressure filtration in dead-end mode at 100 kPa. Membrane fouling resistance was characterized under constant flux
operation using bovine serum albumin (BSA) as a model foulant. The membranes were characterized in terms of morphology, porosity, pore size distribution, energy-dispersive X-ray spectroscopy (EDX), contact angle goniometry, surface free energy and viscosity of the dope solution. Overall, the modified membrane showed increased wettability and reduced surface free energy and pore size. The modified UF membrane with 0.5 wt% NTN loading exhibited improved fouling resistance (fouling rate of 0.58 kPa/ min compared to 0.70 kPa/ min of control membrane) with ~80% water flux recovery. The same membrane showed ~20% increase in water flux and improvement in MWCO and narrower pore size distribution.
1. Introduction

Ultrafiltration (UF) has been widely used to remove suspended solids, proteins, bacteria and macromolecules in various industrial processes including food, dairy, pharmaceutical, biotechnological industries and water/wastewater treatment.\textsuperscript{1, 2} As a consequence of the growing demand, efforts have been focused on improving UF process performance, including feed pre-treatment, membrane materials and module design, and process optimization.\textsuperscript{3} In many cases the key to improved performance processes still relies on the structure and properties of the membrane materials.\textsuperscript{3}

The fast development of techniques and methods for producing nanostructured materials such as nanoparticles or nanotubes has led to breakthroughs in membrane preparation for enhanced solute rejection and solvent permeation.\textsuperscript{4} In particular, attempts to develop organic-inorganic hybrid nanocomposite membranes in which nanoparticles are used as modifiers of polymeric membranes have received much attention.\textsuperscript{5-31} The production of composite membranes by incorporating nanomaterials has resulted in enhanced chemical, mechanical and thermal stability, as well as increased fouling resistance and membrane filtration performance compared to plain polymeric membrane. The improvements are attributed to the changes to the microstructural features (porous structure, and pore size and pore size distribution) of the membranes arising from localized interactions and interfaces between the nanoparticles and the polymer chains during the membrane formation, and altered membrane surface roughness and chemistry.\textsuperscript{4}

The incorporation of nanoparticles (such as metal oxides) into the membrane structures is typically performed by either surface modification route\textsuperscript{5-8} or casting solution blending during the thin film formation.\textsuperscript{9-31} Surface modification of UF membranes can be achieved via surface coating, adsorption or grafting, resulting in enhanced membrane surface wettability, fouling resistance and other surface properties such as surface roughness.\textsuperscript{8}
However, the substantial post-treatment processes are required in surface modification techniques. By contrast, blending the main polymer constituent with additives is simple and straightforward without involving expensive post-processing. Metal oxide nanoparticles used for the modification of polymeric membranes include alumina (Al$_2$O$_3$), silica (SiO$_2$), zirconia (ZrO$_2$), zinc oxide (ZnO), and titania (TiO$_2$). More recently, various porous (0- and 1-dimensional) or layered (2-dimensional) nanomaterials, from conventional mesoporous silica and zeolite to zeolitic imidazolate framework (ZIF), carbon nanotube (CNT), hollow carbon sphere, and clay have been studied for their potential as additives for polymeric membranes. The use of porous nanomaterials could lead to interesting results different from those of conventional dense inorganic materials. The incorporation of porous particles may improve the filler-polymer contact. The polymer chains of diameter about ~1 nm may be able to penetrate into the pores of the particles, hence improving the interface of additive and polymer matrix. In addition, the porous nature of the fillers may give them high affinity to water, which could facilitate water transport through the membrane.

TiO$_2$ nanoparticles have been widely studied as membrane additive due to their natural antibacterial and photocatalytic properties. Membrane incorporated with TiO$_2$ nanoparticles exhibited improved performance in terms of fouling resistance and photocatalytic properties. In most of these studies, TiO$_2$ nanoparticle concentrations above 1 wt% (relative to polymer solution) were used in terms of harnessing their photocatalytic / antibacterial activity. However, the combination with UV irradiation may introduce the risk of polymeric membrane degradation, and UV irradiation is not practicable for hollow fiber or spiral wound membrane modules. High loadings of nanoparticles may be unfavourable considering the aggregation tendency of particles; and membrane pores could be plugged by the particle aggregates during non-solvent induced phase separation (NIPS),
and this could adversely affect the membrane performance. Recently, Sotto et al. used low TiO$_2$ concentrations (below 0.4 wt%) in the membrane fabrication process and improved the flux and fouling resistance of the membrane.\textsuperscript{49} At lower nanoparticle loadings, the tendency of aggregation can be reduced.\textsuperscript{49} However, the membrane performance at a TiO$_2$ nanoparticle loading of below 1 wt\% is still not entirely understood. The study on the low loading of nanoparticles is scarce, and in the case of TiO$_2$ nanoparticles only a few paper have been published.\textsuperscript{49, 51, 52} Therefore, there is a pressing need for an in-depth systematic study into the effects of titania at a concentration of below 1 wt\% on UF membranes. The understanding of such effects is fundamentally important for the development of high-performance of titania-polymer composite membranes for practical applications. In addition, the concern for commercial implementation of TiO$_2$-polymer membranes arises from potential health and environmental risks of TiO$_2$ nanoparticles.\textsuperscript{53-59} The incorporation of TiO$_2$ nanoparticles into membrane may pose secondary contamination to the treated water caused by leaching of TiO$_2$ nanoparticles. As a result, more studies into membrane stability are required to ensure the TiO$_2$-based polymeric membrane can be safely used without posing environmental and health risks.

In this paper, we report on a simple and effective method for preparing nanoporous titania nanoparticles (NTN) as a modifier for PES UF membrane. NTN was produced via a modified hydrothermal reaction, followed by calcination to improve its compatibility with PES. A systematic study of the concentration effect of NTN in concentration range below 1 wt\% relative to dope solution on PES UF membrane was carried out to determine the effect of NTN on the membrane performance. The amount of TiO$_2$ in the membrane-treated water was determined using inductively coupled plasma mass spectrometry (ICP-MS) to investigate the risk of secondary contamination.
2. Materials and Methods

2.1 Materials

Polyvinylpyrrolidone (PVP; 40 kDa), polyethylene glycol (PEG; with MW of 35, 100 and 200 kDa), N-methyl-2-pyrrolidone (NMP), and bovine serum albumin (BSA; 66 kDa) were purchased from Sigma-Aldrich, Australia. TiO$_2$, (Degussa P25, about 20 nm) was purchased from Evonik Degussa Chemicals (Germany). Sodium hydroxide (NaOH) pellets were purchased from Merck Millipore, Australia. Hydrochloric acid was purchased from Ajax Finechem Pty Ltd, Australia. Poly(ethersulfone) (PES; Ultrason E6020P, 51 kDa) was purchased from BASF Co. Ltd., Germany. The water used for the experiments was purified with a water purification system (Milli-Q integral water purification system, Merck Millipore Australia) with a resistivity of 18.2 MΩ/cm. Distilled water was obtained from a laboratory water distillation still (Labglass Aqua III).

2.2 Synthesis of Nanoporous Titania Nanoparticle (NTN)

The synthesis of NTN followed a modified process reported elsewhere.$^{60}$ 1.5 g of P25 was added into 100 ml of 10 M NaOH solution. The suspension was mixed by mechanical stirring and ultrasonication; and added into a 150 ml autoclave. The autoclave was sealed and heated at 120 °C for 24 h, and then cooled to room temperature naturally. The suspension was then washed with excessive 0.1M of hydrochloric acid and then Milli-Q water, the solid product was recovered by repeated centrifugation in water. The recovered product was calcined at 450 °C at a ramp rate of 5 °C per min and holding time of 3 h, and white-coloured NTN were obtained.

2.3 Preparation of the membranes

The PES and PES-NTN nanocomposite membranes were prepared via NIPS at room temperature. Three different concentrations of NTN (0.1 wt%, 0.5 wt% and 1.0 wt%) were
used in this study. For instance, to prepare the PES casting solution with 1 wt% NTN, 0.125 g of PVP powder and 0.250 g of NTN were first added into 20.5 g of NMP and mixed via mechanical stirring and ultrasonication for 1 h to ensure good dispersion. 4.125 g of PES was then added, and the solution was stirred overnight or until the PES was completely dissolved. The solution was left to degas for 8 h before use. Table 1 shows the compositions of the casting solutions.

Table 1. The compositions of the casting solutions for PES and PES-NTN nanocomposite membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>PES (wt%)</th>
<th>PVP (wt%)</th>
<th>NMP (wt%)</th>
<th>TiO₂ (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>16.50</td>
<td>0.50</td>
<td>83.00</td>
<td>0.00</td>
</tr>
<tr>
<td>PES-NTN0.1</td>
<td>16.50</td>
<td>0.50</td>
<td>82.90</td>
<td>0.10</td>
</tr>
<tr>
<td>PES-NTN0.5</td>
<td>16.50</td>
<td>0.50</td>
<td>82.50</td>
<td>0.50</td>
</tr>
<tr>
<td>PES-NTN1.0</td>
<td>16.50</td>
<td>0.50</td>
<td>82.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

The membranes were cast on a glass plate using an adjustable micrometer film applicator (stainless steel blade at a gap of 150 µm, Elcometer, USA) at room temperature. The phase inversion step was carried out by immersing the membrane in a coagulation bath of distilled water for 24 h. The membranes were then removed from the bath, rinsed thoroughly with double-deionized water (DDI) water and stored in fresh DDI water for later use. 0.1 wt%, 0.5 wt%, and 1.0 wt% PES-NTN nanocomposite membranes were denoted as PES-NTN0.1, PES-NTN0.5, and PES-NTN1.0, respectively.

2.4 Characterization of the Nanoporous Titania Nanoparticle (NTN)

The crystal structure of NTN was examined using powder X-ray diffraction (15 mA and 40 kV) at a scan rate of 2°/min and a step size of 0.02° (PXRD; Rigaku MiniFlex 600, Cu Kα radiation, Japan). High resolution transmission electron microscopy (HRTEM) images and
selected-area electron diffraction (SAED) were obtained using a transmission electron microscope (TEM; FEI Tecnai G2 T20 Twin TEM, USA). The dried NTN was observed by scanning electron microscopy (SEM; FEI NOVA NanoSEM 450, USA). To measure Brunauer, Emmett and Teller (BET) surface area of NTN, nitrogen sorption analysis was carried out on a physisorption analyzer (Micromeritics ASAP 2020, USA) at liquid nitrogen temperature, and the sample was degassed at 100°C for 12 h before the measurement. Mesopore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) method. Particle size distribution was obtained by analyzing the FESEM images of the membrane top surface using the Image J (http://imagej.nih.gov/ij/). The image was first filtered and thresholded at the predetermined level T, which corresponds to the grey value between 0 and 255 to account for all the membrane pores. The image was then converted to binary image and analyzed to determine the pore size distribution.

2.5 Membrane characterization

2.5.1 Viscosity of casting solution

The viscosity of the solution was measured at 25 °C using a Haake MARS III rotational rheometer coupled with Haake C35P refrigerated bath with a Phoenix II controller (Thermo Scientific, USA). Shear rate in the range of 10 to 50 s⁻¹ was used. An average of multiple measurements obtained from the program was reported for each sample.

2.5.2 FESEM and EDX analysis

Membrane surface and cross-sectional images were obtained using a field emission scanning electron microscope (FESEM; FEI Magellan 400 and FEI Nova NanoSEM 450, USA). Membrane samples were prepared by drying at room temperature and sputter-coating with a 0.5 nm thickness of Pt (208 HR sputter coater, Cressington, UK). For imaging the cross section, the membrane was fractured in liquid nitrogen to retain the membrane structure. Elemental analysis of the membrane samples was conducted by energy-dispersive
X-ray (EDX) spectroscopy in a Nova NanoSEM 450 (Quantax 400 X-ray analysis system, Bruker, USA).

2.5.3 Contact angle and surface free energy measurement

The water contact angles of the membranes surface were measured using a contact angle goniometer by the sessile drop technique (OCA15, Dataphysics, Germany). Images were taken at 1 s intervals for 10 s. An average of minimum 5 measurements was reported. To calculate the surface free energy of membranes, Owens, Wendt, Rabel and Kaelble (OWRK) method was applied.61 In this method, contact angles against at least two liquids with known parameters are measured. The surface free energy of the membrane was calculated using the OCA15 software package (Dataphysics, Germany). Table 2 shows the parameters of the three liquids used in this work.

**Table 2.** The parameters of OWRK method.61

<table>
<thead>
<tr>
<th>Liquid</th>
<th>SFT (mN/m)</th>
<th>$\sigma_{\text{disp}}$ (mN/m)</th>
<th>$\Sigma_{\text{polar}}$ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milli-Q water</td>
<td>72.10</td>
<td>19.90</td>
<td>52.20</td>
</tr>
<tr>
<td>Glycerol</td>
<td>63.40</td>
<td>37.40</td>
<td>26.00</td>
</tr>
<tr>
<td>Poly(ethylene) glycol (200 Da)</td>
<td>43.50</td>
<td>29.90</td>
<td>13.60</td>
</tr>
</tbody>
</table>

2.5.4 Molecular weight cut-off (MWCO)

MWCO was characterized by measuring the rejection of poly(ethylene glycol) (PEG, 35, 100, and 200 kDa). A total organic carbon analyzer (TOC-LCSH/CSN with an auto-sampler ASI-L, Shimadzu, Japan) was used to measure the amount of organic carbon in permeate to determine the amount of PEG.
2.5.5 Pure water flux measurement

Water flux and flux recovery were measured in a dead-end cell (HP4750 Stirred Cell, Sterlitech, USA). A schematic diagram of the bench-scale flux test setup is shown in Figure 1. The DDI water flux test was performed at 100 kPa and room temperature with an effective membrane area of $1.4 \times 10^{-3}$ m$^2$. The membrane was pre-compacted at 150 kPa for at least 30 min until constant flux was reached. The initial water flux was determined under a constant pressure of 100 kPa, as was PEG rejection when determining the rejection characteristics of the membrane.

2.5.6 Membrane fouling resistance

![Figure 1. Schematic diagram of a bench-scale flux test system. Constant pressure operation was carried out without a pump (route A). In constant flux operation (route B), a pump was used to control the permeate flux. Any pressure changes due to membrane fouling were measured by the two pressure transducers.](image)

Constant flux fouling test was carried out to determine the fouling resistance of the membranes. The membranes were fouled by filtration of BSA (0.5 wt%, pH 7) at a constant flux of 60 l.m$^{-2}$.h$^{-1}$ (LMH) for 50 min using a peristaltic pump (L/S Digital Drive, L/S Easy-
Load 3 pump head, peroxide-cured silicone tubing, L/S 13, Masterflex, USA) and fixed nitrogen gas feed pressure. The transmembrane pressure (TMP) was measured using two pressure transducers. The fouled membranes then underwent an in-place physical and chemical cleaning cycle. For physical cleaning, the membranes in the cell were rinsed with DDI water by half-filling the cell (150 ml), followed by pouring for 2 times. 300 mL of DDI water was then added to the cell and stirred for 15 min. After that, the membrane was rinsed for another 2 times. For chemical cleaning, 100 ml of NaOH solution (0.2 wt%) was added to the cell and stirred for 25 min. After that, the membrane was rinsed twice to wash off the solution. After every cleaning step, the water flux was measured at constant pressure of 100 kPa. Each membrane went through 3 fouling cycles at a constant flux and 3 cleaning cycles.

To evaluate the fouling performance of membranes, flux recovery (FR) of membranes was calculated as follows:

\[
FR(\%) = \frac{J_{AF}}{J_{BF}} \times 100
\]

(1)

where \(J_{BF}\) and \(J_{AF}\) are the pure water flux of the membrane before and after the fouling and cleaning, respectively. Fouling behaviour can be investigated by estimation of resistance of membranes as shown below:

1) Total resistance \((R_t)\)

\[
R_t = R_m + R_r + R_{ir}
\]

(2)

where \(R_m\) is the intrinsic membrane resistance, \(R_{ir}\) is the irreversible resistance, and \(R_r\) is the reversible resistance.

2) Intrinsic membrane resistance \((R_m)\)

\[
R_m = \frac{TMP}{\mu \times J_{BF}}
\]

(3)

where \(TMP\) is the transmembrane pressure, and \(\mu\) is the permeate viscosity.

3) Irreversible resistance \((R_{ir})\)
\[ R_{ir} = \frac{TMP}{\mu \times J_{AF}} - R_m \]  

(4)

where \( J_{AF} \) is the water flux at 100 kPa after physical and chemical cleaning.

4) Reversible resistance (\( R_r \))

\[ R_r = \frac{TMP}{\mu \times J_F} - R_m - R_{ir} \]  

(5)

where \( J_F \) is the BSA filtration flux which was set at 60 LMH in our experiment. TMP was taken after 50 min BSA filtration.

2.5.7 Permeate analysis

The amount of TiO\(_2\) in the permeate was analyzed using a standard method (CM050A and CM050C\(^{62}\) used by Australian Laboratory Services (ALS; http://www.alsglobal.com/). 50 ml of the permeate was collected for each membrane in the first 10 min. The sample was first acid-digested and made up to volume with deionized water, and then analyzed via inductively coupled plasma mass spectrometry (ICP-MS).

3. Results and Discussion

3.1 Structure and morphology of the nanoporous titania nanoparticles (NTN)

NTN was formed from calcination of TiO\(_2\) which form a nanoporous structure with pore size ~20 nm (Figure 2a). Figure 2b shows the HRTEM image of NTN. The lattice spacing of 0.369 nm corresponds to the (101) plane of TiO\(_2\) anatase. The SAED ring patterns (Figure 2c) and XRD (Figure 2d) indicate that the NTN consisted of mostly anatase phase and small portion of rutile phase, which was similar to commercial P25. Figure 2e shows the SEM image of NTN. The sizes of NTNs were mostly less than 100 nm (Figure 2f). NTN had a type IV isotherm with a type H1 hysteresis loop (Figure 2g) and a BET surface area of 105.18 ± 0.34 m\(^2\) g\(^{-1}\) compared to 51.23 ± 0.18 m\(^2\) g\(^{-1}\) of P25. The higher surface area of NTN may
promote better compatibility with PES due to enhanced interaction with PES chains, potentially between hydroxyl groups on the surface of NTN and aryl ether oxygen atom or sulfone oxygen atom in PES. Based on BJH model (Figure 2h), NTN had a pore size distribution around 16-31 nm. The pores, which may be the packing pores or the nanopores in NTNs, may be penetrated by PES chains when mixed with the PES polymer which improve the membrane stability.

Figure 2. (a) TEM image, (b) HRTEM image, (c) SAED, (d) XRD pattern, (e) SEM image, (f) Particle size distribution based on SEM (inset), (g) nitrogen sorption isotherms, and (h) pore size distribution of nanoporous titania nanoparticles (NTN).

3.2 Membrane morphology and surface property

Figure 3 shows the FESEM images of the top surface, bottom surface and cross-sections of the membranes. The top and bottom surfaces of the membranes showed the typical morphology of PES membranes synthesized via NIPS. Using image processing tool (Image J) on the SEM images of the membrane top surface, a membrane surface pore size distribution was obtained (Figure 4). All modified membranes (PES-NTN0.1, PES-NTN0.5 and PES-NTN1.0) show narrow pore size distribution between 2 – 6 nm, compared to 4 – 12
nm of the pristine membrane. That is, the modified membranes have smaller pore radius. Based on these results, lower molecular weight cut-offs (MWCO) of modified membranes are expected. The membranes were dried in air and sputter-coated with 0.5 nm of Pt, thus the pore size obtained via SEM image analysis may appear smaller than the actual pore size of the membrane. However, since all membranes underwent the same drying and coating step, the pore size distribution analysis provides useful information about the membrane top surface, which is not attained via molecular probe rejection experiment. The membrane cross-sections show typical asymmetrical structure, of finger-like structure on the top of the matrix, extending to a sponge-like structure in the sub-layer and macrovoidic bottom layer. All NTN-modified PES membrane show elongated and broader tiny finger-like structures of size 0.4 to 0.7 µm on the top section of the membrane, which extends to larger channels of 3.0 – 7.5 µm. The sponge-like bottom layer on the other hand, becomes thicker with NTN loading. As the loading of NTN were increased, more macrovoids were observed in the sub-layer of the membrane (more pronounced in PES-NTN1.0), and the membrane thickness increased with NTN loading, from ~70 µm to ~100 µm (Figure 5). PES-NTN1.0 exhibited increased large macrovoids and membrane thickness. The bottom surfaces of the modified membranes, especially PES-NTN1.0, showed increased large pores compared to pristine membrane. This might be due to the increased viscosity of the casting solution which slows down the phase inversion process, creating large macrovoids and thus, bigger pores in the bottom layer of the membrane. For PES-NTN0.1 and PES-NTN0.5, the increase in viscosity is less significant compared to the increase in water diffusion during NIPS due to the presence of TiO₂ with higher hydrophilic nature. The rapid water diffusion promotes instantaneous demixing and creates more elongated finger-like pores. The effect near the bottom layer of the membrane is less pronounced which might be due to the migration of TiO₂ to the membrane surface. The porosity and the water uptake of the membrane on the other hand, remained relatively
unchanged after incorporating NTN (Figure 5). This may be due to the nanopores in NTN being filled with PES chains, thus not contributing to the membrane porosity. These interactions not only improve the stability of NTN in the membrane, but also restrict the migration of NTN in the polymer matrix to the filtrate when used, posing secondary contamination.

**Figure 3.** SEM images of top, cross-section and bottom layer of PES and NTN-modified membranes.
**Figure 4.** Surface pore size distribution of control and PES-NTN membrane based on SEM top surface analysis.

**Figure 5.** Porosity, thickness, water uptake and viscosity of control and PES-NTN membrane.

The NTN in the membrane matrix was confirmed using EDX spectrometry (Figure 6). At high magnification, the SEM field of view becomes much smaller, and spotting of nanoparticles from PES matrix can be challenging. Thus, PES-NTN1.0 which has the highest loading of NTN among all samples was analysed. Particles found on PES-NTN1.0 cross-
section (Figure 6) were confirmed using EDX mapping on the whole region, where Ti element was marked in red, indicating the successful incorporation of NTN.

![EDX elemental mapping of PES-NTN1.0 membrane cross section](image)

**Figure 6.** EDX elemental mapping of PES-NTN1.0 membrane cross section. The red region represents the Ti element.

Figure 7 shows the contact angle of various liquid and surface free energy of control and modified membrane. The wettability of NTN-modified PES membrane surfaces was characterized by measuring their water contact angles. The water contact angle of the membranes decreased by around ~15% when NTN were added up to 1 wt%, indicating that the surface of the modified membranes was slightly more hydrophilic compared to the native PES membranes. The increase in wettability might be attributed to the migration of NTN during NIPS. The polyethylene glycol and glycerol contact angles, on the other hand remained relatively unaffected. Based on the contact angles of the 3 selected liquids, the surface free energy was obtained via OWRK method. The surface free energy decreased with increasing loading of NTN from 42.9 mN m⁻¹ for pristine membrane to 40.2 mN m⁻¹ for PES-NTN1.0. The decrease in contact angle and surface free energy may improve the fouling resistance of the membrane by reducing the propensity of membrane to interact with foulant.
Figure 7. Contact angle of various liquid and surface free energy of control and NTN-modified membrane.

3.3 Membrane Performance

3.3.1 Pure water flux

Figure 8 shows the average pure water fluxes at 100 kPa for control and NTN-modified membrane. In general, as the loading increases, the water flux increases. PES-NTN0.5 showed the highest pure water flux of 446 LMH which may be due to increased wettability, reduced tortuosity and increase surface pore density. When NTN was increased to 1 wt%, the improvement over the flux was reduced and flux similar to control membrane was attained. This may be due to the undesirable effect caused by increased NTN agglomeration or pore plugging. Loading beyond 1 wt% as of many reported studies may produce higher flux compared to pristine membrane. However, the flux improvement is more likely due to the increased surface pore size which reduces solute rejection, i.e. flux increase with the loss of solution rejection. In our case, the modified membranes exhibited smaller pore size (Figure 9) and a narrower pore size distribution in smaller pore range (Figure 4) compared to pristine membrane. The abundance of pore in lower range of pore size distribution could be due to the escape of small NTN aggregates during NIPS, while large NTN aggregates remained trapped within the polymer matrix due to restricted mobility and entanglement by PES chains.
3.3.2 Molecular weight cut-off (MWCO)

The rejection of PEG with molecular weight of 100 kDa is shown in Figure 8. The NTN-modified membranes showed higher rejection of 100 kDa, with PES-NTN0.1 having the highest rejection (92.8%). This could be due to two reasons — (1) increased phase exchange rate (demixing rate) near the top surface as NTN have higher affinity to water than PES; (2) migration of small NTN (polymer-poor phase), leaving behind more pores of their own size on membrane surface. The final pore sizes created by such phenomenon may be smaller after completion of NIPS. Molecular weight cut-off curves for the control and NTN-blended PES membranes are shown in Figure 9. The results show that the MWCO (90% PEG rejection) of the membranes shifted below 100 kDa (corresponds to pore size of ~16.5 nm) as NTN loading was increased from 0.1 wt% to 1.0 wt%. Also, the rejections of PEG with molecular weight of 35 kDa were increased for all modified membrane, further confirming the reduced surface pore size. Compared to membrane pore size based on SEM analysis, the pores are larger due to — (1) shrinkage of pores as the membrane was dried; (2) Existence of larger pores or defects that decrease the solute rejection.

**Figure 8.** Pure water flux and rejection of PEG (100 kDa) of control and NTN-modified membrane.
3.3.3 Fouling Resistance

The anti-fouling property of the membranes was investigated under constant flux operation. During the constant flux fouling test, transmembrane pressure (TMP) increases with increasing fouling. A membrane with higher fouling resistance will show slower increase in TMP. The membranes were pre-compacted before the fouling cycle to rule out an increase in TMP due to morphological change of the membrane. Figure 10 shows the change in TMP during 50 min BSA filtration at constant flux of 60 LMH. The actual TMP after 3 fouling cycles are shown in Table 3. From Figure 10a, all modified membranes show lower TMP increases, with PES-T0.5 showing the lowest fouling rate of 0.58 kPa/ min (0.70 kPa/ min for control membrane), followed by PES-NTN0.1 and PES-NTN1.0. This is contributed by the combined effect of reduced contact angle, free surface energy and surface pore size of the modified membrane. After the first fouling and cleaning cycle, the change in TMP remained almost the same for both the control and modified membranes, which indicate that the modified membrane loses its anti-fouling properties after the cleaning process. We speculate that NTN underwent the following reaction in NaOH solution during chemical cleaning process:\textsuperscript{67}
\[ TiO_2(s) + (4 - n)H^+ \rightleftharpoons Ti(OH)_{4-n}^{(4-n)+} + (2 - n)H_2O \]  

where \( n \) refers to the state of Ti(IV) ion hydrolysis. The cleaned membrane therefore loses its anti-fouling properties as TiO2 was converted to titanium hydroxide. For NTN-modified membrane, other chemical cleaning agents besides NaOH solution or low concentration of NaOH solution will need to be used to retain the effectiveness of the modified membrane in fouling resistance.

**Figure 10.** Transmembrane pressure (TMP) change with time (0.5 wt% BSA, pH 7) for the control PES and NTN-modified membranes at constant flux of 60 LMH for 50 min. (a) Cycle 1, (b) Cycle 2, and (c) Cycle 3.

Table 3 shows the flux recovery of the control and modified membrane after 3 cycles of fouling and cleaning. All membranes showed BSA rejection of 95% and above during the fouling tests and flux recovery of ~28 - 35% and ~67 - 80% after physical and chemical cleaning, respectively. The flux recovery remained relatively unchanged after modification. However, the pure water flux of PES-NTN0.5 remained higher than that of the control membrane after 3 fouling cycles.

To quantitatively examine the membrane fouling performance, flux recovery (\( FR \)), intrinsic membrane resistance (\( R_m \)), reversible resistance (\( R_r \)), and irreversible resistance (\( R_{ir} \)) were calculated using Equations (1) – (5). Table 4 shows the filtration resistances of the control and modified membranes. The control PES membrane had highest intrinsic resistance among...
all. The reversible resistance over total resistance ratios ($R_r/R_T$) did not vary much after modification, which were consistent with the overall flux recovery. All modified membranes showed reduced irreversible resistance of the membrane.

**Table 4.** Filtration resistances of control and NTN-modified membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>$R_m$</th>
<th>$R_{ir}$</th>
<th>$R_r$</th>
<th>$R_T$</th>
<th>$R_{ir}/R_T$</th>
<th>$R_r/R_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES</td>
<td>1.08 ± 0.04</td>
<td>0.64 ± 0.10</td>
<td>5.70 ± 0.17</td>
<td>7.42 ± 0.10</td>
<td>0.09</td>
<td>0.77</td>
</tr>
<tr>
<td>PESNTN-0.1</td>
<td>0.99 ± 0.01</td>
<td>0.45 ± 0.17</td>
<td>5.80 ± 0.40</td>
<td>7.24 ± 0.48</td>
<td>0.06</td>
<td>0.80</td>
</tr>
<tr>
<td>PESNTN-0.5</td>
<td>0.91 ± 0.02</td>
<td>0.37 ± 0.08</td>
<td>4.43 ± 0.28</td>
<td>5.70 ± 0.28</td>
<td>0.07</td>
<td>0.78</td>
</tr>
<tr>
<td>PESNTN-1.0</td>
<td>1.07 ± 0.01</td>
<td>0.42 ± 0.05</td>
<td>5.79 ± 0.16</td>
<td>7.29 ± 0.13</td>
<td>0.06</td>
<td>0.79</td>
</tr>
</tbody>
</table>

3.3.4 *TiO$_2$ amount in the permeate*

TiO$_2$ nanoparticles can produce free radical and exert a strong oxidizing ability. To successfully implement the use of TiO$_2$ nanoparticles as additives, the additives must not be released to the permeate during filtration. Table 5 shows the amount of TiO$_2$ of permeates for both control and modified membranes. The result shows that the amount of TiO$_2$ in water is less than 0.001 ppm (or 1 ppb) for all membranes tested. The result confirms that most of the TiO$_2$ used in modifying the membrane is retained in the membrane during filtration. Thus, secondary contamination of the treated water is negligible.

**Table 5.** Amount of TiO$_2$ in the permeate (ppm) for various membranes tested.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of NTN in membrane (wt%)</th>
<th>Amount of TiO$_2$ in permeate (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES</td>
<td>0.0</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>PES-NTN0.1</td>
<td>0.6</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>PES-NTN0.5</td>
<td>2.9</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>PES-NTN1.0</td>
<td>5.7</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

*Based on amount of TiO$_2$ added into the casting solution.*
A systematic study of the filtration performance of NTN-modified membranes provides a more complete understanding of membranes with low concentration of TiO₂ below 1%. Previous reports adopted techniques such as water flow rate method \(^5\) or rely on single molecular probe (BSA) \(^5\) to determine the pore size or the rejection property of modified membrane under low concentration of TiO₂. By using poly(ethylene) glycol of different molecular weight for rejection test, a more accurate pore size of the membranes can be obtained. NTN-modified membranes show a decrease in the pore size and despite the decrease, the modified membrane showed improved flux, which could be due to increased wettability and increased surface pore density. Compared to other systems with similar TiO₂ loading, \(^4\), \(^5\), \(^2\) NTN-modified membranes exhibited improved both flux and rejection. In the work of Wu et al., \(^2\) the improved flux was coupled with increased pore size (reduced rejection). Although rejection test was not carried out, significant increase in the membrane surface pore size was observed in their SEM images.\(^2\) In the case of TiO₂-modified nanofiltration membrane system (with PES concentration between 25 to 32 %), despite the improvement over the flux and fouling resistance, the modified membranes with TiO₂ concentration below 1% exhibited decreased rejection of methylene blue. The poorer rejection could be due to increased pore size and porosity.\(^4\)

Membrane fouling resistance is another important parameter to be considered when determining modified membrane performance. Previous findings for membranes modified with low loading of TiO₂ revealed that the fouling resistance was improved, despite the low loading.\(^4\), \(^5\), \(^2\) However, the long term fouling resistance of the modified membranes was not known. The early studies relied on single fouling test and no chemical cleaning method was used to remove the foulants on the membrane surface. We addressed these by adopting a more complete fouling test. Our results are in agreement with the aforementioned\(^4\), \(^5\), \(^2\) and further confirmed the fouling resistance improvement. The improvement was not observed
after the first cycle which could be due to the chemical reaction with the cleaning agent (NaOH). Taking all the findings available into consideration (of the other groups and this work), the low concentration approach is promising. By further using porous material in low concentration, we are able to improve not only the flux and fouling resistance of the modified membranes, but also their rejection properties.

One possible drawback of such inorganic-blended polymeric membrane is the potential leaching of additives in the membranes when used. The leaching potential needs to be investigated before the implementation of these membranes in separation process as the leaching of inorganics may cause secondary contamination to the permeate. However, such study is not available in the case of TiO₂-blended polymeric membrane. Even though the concentration of NTN used in this work is comparably low, the potential of releasing the NTNs into the treated water cannot be ruled out. The trapped NTNs in the membrane matrix may be released when the filtration system is pressurized, altering the structure of the membrane due to compaction. Our results indicated that the amount of TiO₂ in permeates was similar to the feed water and thus the membranes are safe to be used for filtration.

4. Conclusions

PES membranes were modified with low concentrations of nanoporous titania nanoparticles (NTNs) (between 0.1 wt% and 1 wt% relative to dope solution) in the membrane fabrication process. NTN-modified membranes showed improved flux, reduced pore size distribution, and improved solute rejection. The anti-fouling properties of the modified membranes were also improved due to decreased contact angle, surface free energy and pore size. Among all membranes, PES-NTN0.5 showed the highest improvement, with water flux reaching 446 LMH and MWCO less than 100 kDa. The same membrane also showed the highest fouling resistance (fouling rate of 0.58 kPa/ min compared to 0.70 kPa/ min of control membrane) with overall flux recovery of ~80 % after 3 fouling cycles under
constant flux operation. The amount of TiO$_2$ in the permeate from the modified membranes did not increase with NTN loading, and thus the incorporation of NTN did not cause secondary contamination to treated solution. The strategy for incorporating a low concentration of NTN is promising for the fabrication of polymer ultrafiltration membranes with improved membrane performance.
Table 3. Water flux, TMP and flux recovery after 3 cycles of fouling-cleaning experiments for control and modified membranes. NTN: nanoporous titania nanoparticles.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Water Flux (LMH)</th>
<th>Flux&lt;sup&gt;a&lt;/sup&gt; (kPa)</th>
<th>TMP&lt;sup&gt;b&lt;/sup&gt; (kPa)</th>
<th>Flux recovery after physical cleaning (%)</th>
<th>Flux recovery after chemical cleaning (%)</th>
<th>Overall flux recovery after physical cleaning (%)</th>
<th>Overall flux recovery after chemical cleaning (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES</td>
<td>375.3 ± 13.3</td>
<td>100.9 ± 1.4</td>
<td>40.4</td>
<td>35.7</td>
<td>29.9</td>
<td>84.5</td>
<td>78.0</td>
</tr>
<tr>
<td>PES-NTN0.1</td>
<td>407.7 ± 2.9</td>
<td>98.5 ± 6.5</td>
<td>28.6</td>
<td>26.4</td>
<td>27.2</td>
<td>75.8</td>
<td>64.7</td>
</tr>
<tr>
<td>PES-NTN0.5</td>
<td>446.0 ± 12.1</td>
<td>77.6 ± 3.9</td>
<td>37.0</td>
<td>30.0</td>
<td>30.4</td>
<td>80.9</td>
<td>83.2</td>
</tr>
<tr>
<td>PES-NTN1.0</td>
<td>376.3 ± 2.08</td>
<td>99.1 ± 1.7</td>
<td>31.4</td>
<td>30.3</td>
<td>28.8</td>
<td>78.1</td>
<td>73.1</td>
</tr>
</tbody>
</table>

<sup>a</sup> constant pressure of 100 kPa.

<sup>b</sup> final TMP after 50 min BSA filtration.
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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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nanoporous titania

polyethersulfone (PES)

↑ flux
↑ solute rejection
↑ fouling resistance