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Synthesis and Characterization of MWNT/Chitosan and MWNT/Chitosan-Crosslinked Buckypaper Membranes for Desalination

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Abstract:

Novel buckypaper (BP) membranes for nanofiltration application were fabricated from multi-walled carbon nanotubes (MWNT) and biopolymer containing quaternary amine groups (chitosan and chitosan-crosslinked by in-situ amine crosslinking). Characteristics of the BP membranes were systematically characterized in terms of mechanical (tensile strengths varied between 49 ± 4 and 59 ± 3 MPa) and electrical properties (60 ± 1 to 70 ± 1 S/cm), contact angle (76 ± 3° to 102 ± 3°), surface morphology, membrane swelling, pore size, surface charge, solubility, water permeability (ranging from 019 ± 0.01 to 0.87 ± 0.03 L m⁻² h⁻¹ bar⁻¹), and salt rejection (80 - 95% for MgCl₂, 21 - 63% for NaCl, 18 - 37% for MgSO₄ and 6 - 14% for Na₂SO₄). These BP membranes were able to sustain up to 18 bar of pressure. Their properties were significantly affected by the type of biopolymer modifiers. The highest water permeability was obtained with the MWNT/chitosan BP membrane, while the MWNT/chitosan-crosslinked membranes showed the best salt rejection performance. In addition, these BP membranes achieved considerable salt rejection. In addition, separation performance by these membranes appeared to be governed by the unhydrated radii of these inorganic salts.

Keywords: Carbon nanotube, nanofiltration membrane, buckypapers, chitosan, desalination.

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1. Introduction

Carbon nanotubes (CNTs) have attracted significant scientific attention in recent years. They are promising materials for the fabrication of functional membrane materials due to their excellent electrical, mechanical, thermal properties and high surface area [1-5]. For example, molecular dynamic simulations of CNTs membranes have demonstrated unexpectedly much higher water permeability comparing to other known porous materials [6, 7]. As a result, CNTs matrices have been evaluated for membrane applications. Hinds et al. [8] constructed an array of aligned carbon nanotubes (CNTs) incorporated across a polymer film to form a well-ordered nanoporous membrane structure. They observed a permeation fate of four to five times higher compared to conventional fluid flow calculated by the Hagen–Poiseuille equation. In another study, aligned CNTs in silicon nitride composite membranes were fabricated using chemical vapor deposition by Holt et al. [9]. The CNTs in silicon composite membrane achieved faster gas and water permeation than would be expected. However, preparing aligned CNTs is still limited to small-scale, costly and difficult to reproduce techniques [4, 10].

As an alternative to the aligned structure, CNTs can be dispersed in an aqueous solution using sonicator and dispersant and reform to obtain composite thin membrane with fast transport rate and easy to scale-up operation. Recent research has significantly improved the mass transport rate of non-aligned CNTs membranes. For instance, single walled carbon nanotubes (SWNT) with poly(imid siloxane) nano-composite membranes were prepared by Kim et al. [11] and they reported that the mass transport rate of O$_2$, N$_2$ and CH$_4$ increased by increasing SWNTs content in the nano-composite membranes. Polyvinyl alcohol (PVA) was coated with a nonporous hydrophilic polymer and oxidized multi-walled carbon nanotubes (MWNT) nano-composite membranes were fabricated by Wang et al. [12]. Their results showed considerable improvement in the water flux and solute rejection.

Recent investigations have shown that buckypaper (BP) fabricated from aligned arrays of CNTs can have a free volume of up to 70% of the total porous network structure. Potential applications of BP membranes have been explored in several fields including artificial muscles, hydrogen storage, sensors, actuators, for structural
reinforcement in polymer composites and in the membrane separation process [13, 14]. CNTs BP membranes have high permeability towards water and gases as well as good selectivity between small and large molecules [15, 16]. The internal structure of BPs contains small and large pores due to the spaces between bundles of CNTs, while the pore size distributions of BPs are controlled by the pores with diameters of 100 nm or above [17]. The sizes of the BP pores are wholly dependent on the arrangements and sizes of the CNTs. BPs can also absorb gas and liquid to 60 – 70% of their volume because of intrabundle pores and interbundle gaps. This porosity, coupled with high strength, rigidity and exceptional flow rates, suggests that BPs could make outstanding membranes [18].

CNTs have the tendency to aggregate. Thus, a dispersant is required to solubilize for the fabrication of BP membranes. Several studies have used chitosan as a dispersant for preparing a CNTs BP membranes due to their ability to interact with CNTs to form an aqueous solution [19, 20]. Chitosan is a polymer of randomly distributed α-(1-4)-linked D-glucosamine and N-acetyl-D-glucosamine. Chitosan is commercially made by deacetylation of chitin from the exoskeleton of crustaceans. The degree of deacetylation (DDA) controls the solubility of chitosan in acidic solution, the ability to modification supramolecular structures through hydrogen bonding [21]. Chitosan addition allows for BP membrane preparation using solvent evaporation with a low concentration of organic acid such as acetic acid [22, 23]. Several studies have also reported that chitosan can be modified via chemical modifications to create functional derivatives of chitosan [22-25]. These modifications could enhance the mechanical strength, chemical stability, biocompatibility and hydrophilicity of chitosan. For example, the cross-linking of chitosan by dialdehydes [26] or epoxides [27, 28] may lead to a denser network structure, enhancing the mechanical properties and improving the resistance of the membrane against acid, alkali and chemical.

This study reports the fabrication and characterisation of three BP membranes prepared from MWNTs and biopolymer dispersants namely chitosan, chitosan-glycerin (CHIT-glycerin) and chitosan-polyethylene glycol diglycidyl ether (CHIT-PEGDE). Water flux and rejection characteristics of these BP membranes were investigated under
different experimental conditions. Key parameters that control the optimization of these
BP membranes were also systematically examined.

2. EXPERIMENTAL

2.1 Materials

Unfunctionalised thin MWNTs (Nanocyl™ 3100) were obtained from Nanocyl, Belgium. All MWNT samples had 95% purity and were used without any further purification. Low molecular weight chitosan with a deacetylation degree of 82% and a viscosity of 200–800 cP (1% in 1% acetic acid) was obtained from Sigma-Aldrich. Glacial acetic acid with 99.7% purity was purchased from Asia Pacific Specialty (APS) Chemicals Limited, Australia. Glycerin was obtained from Sigma-Aldrich, United States. Polyethylene glycol-diglycidyl ether (PEGDE) (Mn ~526) was obtained from Sigma-Aldrich and they were used for crosslinking chitosan. On the other hand, NaCl, MgCl₂, and Na₂SO₄ were purchased from Sigma-Aldrich. Anhydrous MgSO₄ was purchased from Scharlau, Spain. HCl, methanol and ethanol were bought from Ajax Finechem Pty Ltd., Australia. The filter for MWNT dispersions comprised of rectangular pieces of polyvinylidene fluoride (PVDF) from Millipore (Ireland) in the form of a hydrophobic commercial membrane with a nominal pore size of 0.22 µm. Another hydrophobic PTFE membrane filter with pore sizes 5.0 µm was also purchased from Millipore (Ireland) and used to remove any particulates from the chitosan solution. All the solutions and dilutions in this study were prepared using Milli-Q® water (resistivity of 18.2 MΩ cm).

2.2 BP membrane preparation

2.2.1 Preparation of chitosan crosslinking BP membranes

The chitosan solutions were prepared by dissolving 6 g of chitosan (0.2% w/v) in 3 L of an aqueous solution containing 1% (v/v) acetic-acid. The solutions were heated for 3 h at 80 °C and stirred for 24 h until the chitosan dissolved completely. The solutions were then left overnight to cool at 21 °C. The homogenous solutions were filtered through a 5.0 µm hydrophobic PTFE membrane to remove any undissolved chitosan particles. The final homogenous solution after filtration was divided into three groups.
(i) Chitosan: This was prepared with the homogenous chitosan solution (0.2% w/v) without any additives.

(ii) Chitosan-glycerin: This was prepared with the homogenous chitosan solution (0.2% w/v) and 0.8 g of glycerin (20% chitosan mass).

(iii) Chitosan-PEGDE: This was prepared with chitosan (0.2% w/v) and 0.8 g of PEGDE (20% chitosan mass). Each of these two solutions was heated for 2 h at 50–70 °C, stirred 24 h and left overnight to cool at 21 °C.

MWNTs (15 mg) were added to 15 mL of each chitosan, chitosan-glycerin and chitosan-PEGDE solutions and mixed by sonication for 30 min. The above procedure was repeated 10 times to produce 150 mL of the MWNT dispersion solution. Each dispersion solution was diluted up to 250 mL and then filtrated through hydrophobic PVDF filter paper (142 mm, pore size 0.22 µm) using a vacuum pump at 30–40 mbar. The top of the filtration system (custom-built transport cell unit) was covered with aluminum foil to avoid evaporative loss. The large BP membrane produced on the filtration sheet was placed to dry between absorbent paper sheets with small, flat glasses at the top and left for 24 h at 21 °C. The dry BP membrane was then peeled from the filtration sheet.

2.3 Characterisation techniques and instrumentation

The following instrumentation methods were adopted to analyse and characterise different properties of the BP membranes.

2.3.1 UV-vis-NIR spectroscopy

The absorption of all dispersion solutions (MWNT/chitosan, MWNT/chitosan-glycerin and MWNT/chitosan-PEGDE) was examined from 300–1000 nm using a Cary® 500 UV-vis-NIR spectrophotometer. All above dispersion solutions (0.1 mL) were diluted in a small vial (20 mL) by Milli-Q water (15 mL). The dispersion solutions were taken into a quartz cuvette (1-cm path length) and spectra were measured at estimated 21 °C.
2.3.2 Electrical conductivity

The electrical resistance of three BP membranes was measured at room temperature (21 °C and 45% RH) through using the two-point probe method [29]. All BP samples were prepared via cutting them into small thin strips of 4 mm × 30 mm. Thicknesses of all samples were also determined with a Mitutoyo Digital Micrometer, and width was estimated by optical microscope. The membrane strips were then placed on glass slides using double-sided tape. Both Silver paint (SPI-paint 05002-AB) and copper tape (3M #1181 electrical tape) were used to ensure low contact resistance. The sample-electrode contacts were located under standard compression (10^5 Pa) by using bull clips. Another glass slide was clamped over the membrane using bull clips to be sure continuous connection during the analysis.

An arbitrary waveform generator (Agilent 33220A) was utilize to apply a stepwise DC-voltage ramp from −0.1 to +0.1 V. The current (I) and voltage (V) responses were estimated using a digital multimeter (Agilent 34410A). Measurements were restated for at least five channel lengths from 0.5–3 cm. Electrical resistance as a function of changed length was measured using Ohm's law. This was repeated minimum of five different lengths for each sample to determine the resistance.

2.3.3 Contact-angle measurement

The hydrophobicity of membrane is commonly determined by measuring the contact angle of a water droplet on its surface. The contact angles of all buckypaper membranes were examined using the sessile drop method and a DataPhysics® SCA20 Goniometer fitted with a digital camera. All samples (4 mm × 35 mm) were clamped flat on a glass microscope slide and 2-µL water (Milli-Q, Millipore) droplets were located on the surface of the membranes.

2.3.4 Membrane swelling

BP membranes were cut into thin strips (4 mm × 10 mm) and their thicknesses were determined with a Mitutoyo Digital Micrometer. The weight of each sample was measured using a digital balance (Mettler XS 64). The samples were immersed and kept
for 24 h at 21 °C in different solutions (water/acetic acid at 1, 3 and 5% w/v) and 3 M of sodium hydroxide solution. The strips were taken out at regular intervals, blotted to remove excess liquid and weighed. The degree of swelling (SW%) is calculated using:

\[
SW\% = \frac{W_s - W_o}{W_o} \times 100\%
\]  

(1)

where \( W_s \) is the weight of swollen BP membrane and \( W_o \) is the weight of the dry membrane.

### 2.3.5 Scanning electron microscope

BP membrane morphology was obtained using a JEOL JSM-7500FA SEM at the Electron Microscopy Centre of the University of Wollongong. BP membrane samples were dried in an oven (Binder) at 50 °C for 24 h, and the non-conductive material was coated with gold to improve imaging. They were then mounted onto a brass stub using conductive carbon tape. A 5-kV electric field was used for the measurement. To examine the cross-sectional images, the samples were frozen in liquid nitrogen and carefully snapped open to expose the interior.

### 2.3.6 Mechanical testing

Tensile testing was carried out using a Shimadzu EZ-S tensile tester. Five strips (approximately 4 mm × 10 mm) of a BP membrane sample were used and their thickness was measured using a Mitutoyo IP65 Digital Micrometer. The membrane samples were then located between two parallel plates at 21 °C and 45% RH.

### 2.3.7 Surface area and pore-size distributions of membranes

The surface areas and pore-size distributions of the BP membranes were estimated using a Micrometric ASAP-2020 analyser at King Abdulaziz City for Science and Technology (KACST), Saudi Arabia. The BP samples were cut into small pieces (2 × 2 mm) and then de-gassed at 80 °C for 16 h under vacuum before being tested. The surface areas and pore volumes were determined for all BP membranes by nitrogen adsorption/desorption technique at 77 K. Nitrogen adsorption/desorption isotherms were performed using the Brunauer, Emmett, Teller (BET) method to determine the sample
surface areas [30]. The N\textsubscript{2} isotherms were employed to calculate both small and large pore sizes of the sample using the Barret, Joyner and Halenda (BJH) [31] and Horvath-Kawazoe (HK) [32] methods.

### 2.3.8 Zeta Potential

Surface charge of the BP membranes was examined using a SurPASS electrokinetic analyser (Anton-Paar GmbH, Graz, Austria). Zeta potential (ZP) measurements were conducted using 1 mM KCl of background electrolyte solution. HCl and KOH solutions were used to adjust the pH by automatic titration.

### 2.3.9 Permeability and salt-rejection behaviors

Measurements of water permeability and salt rejection by the investigated BP membranes were carried out using a laboratory-scale crossflow NF/RO (Fig. 1). Milli-Q\textsuperscript{®} water was applied to all membranes at a pressure of 22 bar to compact the membranes before conducting the filtration experiments. Compression of the membranes was carried out for almost 1 h until a steady baseline flux was attained. After the compacting process, permeate flux of DI water was determined at different applied pressures to calculate the water permeability of the membranes. Salt rejection was determined using each individual salt solution (i.e., NaCl, MgSO\textsubscript{4}, MgCl\textsubscript{2}, and Na\textsubscript{2}SO\textsubscript{4}) of 2 g/L separately. The crossflow velocity was set at 34.7 cm/s (cross flow of 100 L/h). The temperature of the feed solution was maintained at 20 ± 2 °C throughout the experiment with the help of a chiller (Series Water Chiller 001-D081 ISS E, Aquacooler, Australia).
The effective membrane area was approximately 40 cm². A standardized conductivity and pH meter (Thermo Scientific™ conductivity meter Orion 4-Star™, Singapore) was used to estimate various salt concentrations (NaCl, MgSO₄, MgCl₂ and Na₂SO₄) in the feed and permeate water. The percentage observed rejection ($R_o\%$) of the salts is determined from the permeate and feed samples using the following equation [33]:

$$R_o\% = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

where $C_p$ and $C_f$ are salt concentrations on the permeate and the feed streams respectively.
Initially, this experiment was carried out at a crossflow velocity of 34.6 cm/s by determining the pure-water flux, followed by the addition of the salt into the feed solution to prepare 2 g/L (concentration of salt) and measurement of the permeate water flux and permeate salt concentration. This step was measured at 10 and 16 bar of applied pressure. To evaluate the influence of the solution pH salt rejection, the solution pH was incrementally increased to pH 10 by adding a small volume of 1 M KOH and then incrementally decreasing the pH by dropwise addition of 1 M HCl.

3. RESULTS AND DISCUSSION

3.1 Dispersion of MWNT using Chitosan and Chitosan-crosslinked

Three solutions (chitosan, chitosan-glycerin and chitosan-PEGDE) were successfully used to prepare MWNT dispersions to fabricate BP membranes. UV-vis-NIR spectroscopy was used to compare non-crosslinked and crosslinked chitosan for dispersing MWNTs (Fig 2.A). The absorbance of MWNT/chitosan dispersion was measured at wavelengths of 300–1000 nm. This absorbance was amplified by increasing the sonication time, which is consistent with previous studies in the literature [15, 16, 20]. In Fig 2.B, the absorbance of the dispersions at 660 nm was plotted as a function of sonication time. This wavelength (660 nm) was chosen to avoid absorbance attributable to dispersant (chitosan or crosslinked chitosan) and the solvent (Milli-Q water). Results in Fig 2.B suggest that 10 min sonication was sufficient for good dispersion of the MWNT in the solution containing chitosan and/or chitosan-glycerin, whereas 20 min sonication was necessary to disperse MWNT in the solution containing chitosan-PEGDE. The results in Fig 2.B suggest that 20 min is a suitable amount of time to disperse the MWNT in both solutions (chitosan and crosslinked chitosan). Accordingly, sonication time of 20 min was chosen to ensure significant dispersion of the MWNTs.
Fig 2. A) UV-vis spectra of MWNT/chitosan dispersion as a function of sonication time and B) comparison of the effect of increasing sonication time on the absorbance at 660 nm of MWNT/chitosan, MWNT/chitosan-glycerin and MWNT/chitosan-PEGDE dispersions.

3.2 Electrical properties of BP membranes

The membrane conductivity can potentially be regulated by an electric potential to improve separations performance [34]. Consequently, the electrical properties of the BP membranes were investigated. The I-V characteristics of MWNT/chitosan, MWNT/chitosan-glycerin and MWNT/chitosan-PEGDE dispersions membranes were determined using the two-point probe method under ambient conditions of 21 °C and 45 % relative humidity. All BP membranes showed linear I–V characteristics, indicating ohmic behavior (Fig 3).
Fig 3. Resistance as a function of sample length for three different BP membranes.

The electrical conductivity of MWNT/chitosan and MWNT/chitosan-crosslinked (chitosan-glycerin and chitosan-PEGDE) was determined from the linear regression of resistance against length (Fig 3) using equation 3 [15, 20]:

$$R_T = \frac{1}{\sigma A} l + R_c$$  \hspace{1cm} (3)

$R_T$ is the total resistance of BP membranes, which related to its length ($l$) and $\sigma$ is the conductivity of the BP membranes. $A$ is the cross section area of the sample. The conductivity value in Table 1 ($70 \pm 1$ S/cm) of MWNT/chitosan was slightly higher than that of the MWNT/chitosan-crosslinked (MWNT/chitosan-glycerin ($66 \pm 1$ S/cm) and MWNT/chitosan-PEGDE ($60 \pm 1$ S/cm)) membranes. The chitosan-crosslinked as a dispersant did not significantly affect the electrical conductivity of the MWNTs. It is noted that the conductivity values of MWNT/chitosan and MWNT/chitosan-crosslinked BP membranes investigated here were higher than to those seen previously with Trix or Cipro (Table 1) [16]. For example, the conductivity values of the MWNT-Trix and MWNT-cipro BPs were $24 \pm 16$ and $42 \pm 1$ S/cm respectively (lower than those of the three investigated membranes). Therefore, results in Table 1 suggest that the conductivity of BP membranes (MWNT/chitosan and MWNT/chitosan-crosslinked) is not affected by the concentration of these biopolymers (chitosan and chitosan-crosslinked).
Table 1. Physical properties of MWNT-chitosan and MWNT-chitosan-crosslinked BP membranes.

<table>
<thead>
<tr>
<th>BP membrane</th>
<th>Contact angle (°)</th>
<th>Conductivity S/cm</th>
<th>Thickness (µm)</th>
<th>Elongation (%)</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Toughness J/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/Trix a</td>
<td>55 ± 10</td>
<td>24 ± 16</td>
<td>-</td>
<td>1.3 ± 0.2</td>
<td>6 ± 3</td>
<td>0.6 ± 0.3</td>
<td>0.1 ± 0.03</td>
</tr>
<tr>
<td>MWNT/cipro a</td>
<td>41 ± 5</td>
<td>42 ± 1</td>
<td>-</td>
<td>0.5 ± 0.2</td>
<td>6 ± 2</td>
<td>1.3 ± 0.1</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>MWNT/τ-carrageenan b</td>
<td>77 ± 1</td>
<td>-</td>
<td>-</td>
<td>3.4 ± 0.6</td>
<td>24 ± 1</td>
<td>2.7 ± 0.7</td>
<td>-</td>
</tr>
<tr>
<td>MWNT/chitosan</td>
<td>102 ± 3</td>
<td>70 ± 1</td>
<td>52 ± 3</td>
<td>5.7 ± 0.5</td>
<td>56 ± 3</td>
<td>2.9 ± 0.1</td>
<td>2.1 ± 0.3</td>
</tr>
<tr>
<td>MWNT/chitosan-glycerin</td>
<td>80 ± 2</td>
<td>66 ± 1</td>
<td>52 ± 6</td>
<td>6.4 ± 2</td>
<td>49 ± 4</td>
<td>2.8 ± 0.2</td>
<td>2.2 ± 0.8</td>
</tr>
<tr>
<td>MWNT/chitosan-PEGDE</td>
<td>76 ± 3</td>
<td>60 ± 1</td>
<td>58 ± 4</td>
<td>8.1 ± 2</td>
<td>59 ± 3</td>
<td>2.7 ± 0.2</td>
<td>2.3 ± 0.2</td>
</tr>
</tbody>
</table>

Values obtained are the average of at least five samples, with the errors estimated from the standard deviation of measurements. a Data for MWNT/Trix and MWNT/cipro taken from reference[16]. b Data for MWNT/τ-carrageenan taken from reference[42].

3.3 Wettability of BP membranes

Hydrophobicity provides information about the nature of the membrane surface, and contact angle determines the hydrophobicity; that is, if the contact angle is high, the material is hydrophobic. The MWNT/chitosan (un-crosslinked chitosan) BP membrane has a significantly higher contact angle (102 ± 3°) than all the other BP membranes in Table 1 including those containing cross-linked chitosan (MWNT/chitosan-glycerin and MWNT/chitosan-PEGDE). Contact angle results in Table 1 also indicate that the MWNT/chitosan BP membrane has a hydrophobic surface (i.e. less likely to adsorb or be wetted by water). However, the contact-angle values for the MWNT/chitosan-glycerin and MWNT/chitosan-PEGDE (crosslinked chitosan) BP membranes were 80 ± 2° and 76 ± 3° respectively, showing hydrophilicity. The high contact-angle value of the MWNT/chitosan BP suggests that most of the membrane's surface consisted of MWNT. It is likely that some of the chitosan was lost during the filtration process. The contact
angles of the three BP membranes are also consistent with their respective conductivity results (Table 1), MWNT/chitosan exhibited the highest conductivity. This could also indicate that there was a greater proportion of MWNT on its surface than on the other membranes. Moreover, the obtained contact-angle values (Table 1) were significantly higher than those of other studies. For example, the contact angle values of the MWNT/chitosan composite membranes decreased from 86° to 56.5° [35]. In addition, Table 1 shows that the contact angle of the MWNT buckypapers fall within the range 76 ± 3° to 102 ± 3°. This is a significantly high values compared to those reported previously (Table 1) for the MWNT dispersed with different dispersants (cipro and Trix) [16]. This is indicated that the contact angle values of BP membranes (MWNT/chitosan and MWNT/chitosan-crosslinked) are affected by using biopolymers such as chitosan and chitosan-crosslinked as dispersants.

3.4 Morphology of BP membranes

SEM images of the three BP membranes (MWNT/chitosan, MWNT/chitosan-glycerin and MWNT/chitosan-PEGDE) are shown in Fig 4. MWNT (0.1% w/v), chitosan (0.2% w/v) and glycerin or PEGDE (20% by weight relative to chitosan) were used. In the case of MWNT/chitosan-crosslinked BP membranes (Fig 4C and E), nanopore formation occurs during the crosslinking method. In other words, these BP membranes fabricated with dispersions containing MWNT/chitosan-glycerin or MWNT/chitosan-PEGDE exhibit pore formation. This pore formation is related to phase separation through the crosslinking method, which generally occurs when chitosan is crosslinked in the presence of glycerin or PEGDE [36, 37]. Thus, pores formation at the surface can be observed in the SEM images of MWNT/chitosan-PEGDE (Fig 4E). Also, lesser pores are observed in the images of MWNT/chitosan-glycerin (Fig 4C). This indicates that the pores on the surfaces of the BP membranes are highly dependent on the identity of the dispersants used. In contrast, the MWNT/chitosan (Fig 4A) revealed a randomly entangled mat/network of MWNTs with small-sized pores between bundles of nanotubes. Moreover, the SEM images of the three BP membranes show that the MWNTs are well dispersed through the chitosan and crosslinked chitosan solutions (i.e. there are no many aggregates). However, it is clear from the SEM images (Fig 4A, C and E) that the BP
membranes had much larger agglomerates of nanotubes with small numbers of irregularly sized pores compared to those of the BP membranes formed from MWNT/Trix [16, 38]. Whitten et al.[39] had similar results for single-walled nanotubes (SWNTs) membranes, showing that biopolymers (chitosan) can suspend much larger agglomerates of nanotubes than low-molecular-weight (Trix) dispersant because of their greater molecular weights. Additionally, the SEM images of cross section (Fig 4B, D and F) show that there is no difference in the structures of the fractures of the three buckypaper membranes, all showing numbers of the MWNTs layers in their structure, except for the few different numbers of MWNTs layers. With providing very narrow spaces between MWNTs and more contents of MWNTs were found from the surface layer.
Fig 4. SEM images of the surface and cross-section morphology of the three BP membranes: A and B) MWNT/chitosan BP; C and D) MWNT/chitosan-glycerin BP; and E and F) MWNT/chitosan-PEGDE BP obtained at 50 KV magnification; BPs were fabricated from dispersions made by sonicing samples containing 0.1% (w/v) MWNTs and different dispersants (chitosan, chitosan-glycerin and chitosan-PEGDE) for 30 min.

3.5 Mechanical characteristics

Mechanical strength is a critical property in determining the usability of BP membranes for filtration. Typically, straightforward strategies were used to detect high-
performance engineering polymers for membrane materials, to improve crosslinked polymers or to produce polymer composite membranes [40, 41]. In this work, tensile stress–strain curves of the MWNT/chitosan and MWNT/chitosan-crosslinked membrane samples were developed as discussed earlier and are shown in Fig 5. The values of the tensile properties (i.e. elongation, tensile strength, Young's modulus and toughness) are summarised above in Table 1. These properties for the three BP membranes fell within a relatively small range of values. For example, the tensile strength of MWNT/chitosan-PEGDE (59 ± 3 MPa) was slightly higher than for MWNT/chitosan (56 ± 3 MPa) and MWNT/chitosan-glycerin (49 ± 4 MPa). Moreover, MWNT/chitosan-PEGDE BP had the lowest value of Young's modulus, at 2.67 ± 0.19 GPa. The values for MWNT-chitosan were 2.91 ± 0.11 GPa, and 2.82 ± 0.19 GPa for MWNT/chitosan-glycerin. In contrast, the elongation-to-break value for the MWNT/chitosan BP membranes was 5.7 ± 0.5%, which is lower than the values obtained for both of the crosslinked membranes (i.e. 8.1 ± 2% and 6.4 ± 2% for the MWNT/chitosan-PEGDE and the MWNT/chitosan-glycerin membranes respectively). The toughness value of the MWNT/chitosan-PEGDE BP membrane was highest (3.8 ± 0.8 J/g). These enhanced mechanical properties can be attributed to the addition of PEGDE (cross-linking agent), which may be bonded with amino groups of chitosan [24]. Further, all the mechanical properties reported here were much higher than the mechanical properties of BPs prepared by the vacuum-filtration method using MWNTs and various dispersions, such as Trix, cipro and τ-carrageenan as summarized in Table 1 [16, 42]. A previous investigation supports this hypothesis, showing that only when high molecular mass dispersants, such as polysaccharides and proteins, were included in the membrane, was there a significant increase in the strength of SWNT BPs [20].
3.6 Solubility

Chitosan is easily soluble in water at ales than pH 6.5 due to a primary amine group in its structure with the capacity for pronation and formation of a water-soluble substance. Therefore, crosslinking treatment is required to reinforce the chemical stability of chitosan membranes in low-pH or acidic solutions. It is well known that chitosan can be chemically crosslinked with a variety of crosslinking agents [24, 43]. Ngah et al. [43] reported that the crosslinked chitosan was insoluble. In this study, the solubility behaviours of MWNT-chitosan and MWNT-chitosan-crosslinked BP membranes were determined and are summarized in Table 2. The solubility results showed that the MWNT combined with pure chitosan (not cross-linked MWNT/chitosan) was soluble in acidic solution but insoluble in Milli-Q water and NaOH solution. This is because chitosan has a primary amine group (–NH₂) that makes it easily soluble in dilute acid solutions [43]. However, after crosslinking, MWNT-chitosan-glycerin and MWNT/chitosan-PEGDE membranes were insoluble in Milli-Q water and acidic and alkaline solutions (Table 2). In addition, the results reported in this work for the solubility of MWNT/chitosan and MWNT/chitosan-PEGDE are consistent with results obtained in a previous study on chitosan and cross-linked chitosan (chitosan-PEGDE) [43].
Table 2. Solubility effect of MWNT-chitosan and MWNT-chitosan-crosslinked BP membranes tested on their solubility in 1–5% (v/v) acetic acid, Milli-Q water and 3-M sodium hydroxide.

<table>
<thead>
<tr>
<th>BP membrane</th>
<th>Solvent</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Milli-Q water</td>
<td>Acetic acid 1% (v/v)</td>
<td>Acetic acid 3% (v/v)</td>
<td>Acetic acid 5% (v/v)</td>
<td>NaOH 3 M</td>
</tr>
<tr>
<td>MWNT/chitosan</td>
<td>insoluble</td>
<td>soluble</td>
<td>soluble</td>
<td>soluble</td>
<td>insoluble</td>
</tr>
<tr>
<td>MWNT/chitosan-glycerin</td>
<td>insoluble</td>
<td>insoluble</td>
<td>insoluble</td>
<td>insoluble</td>
<td>insoluble</td>
</tr>
<tr>
<td>MWNT/chitosan-PEGDE</td>
<td>insoluble</td>
<td>insoluble</td>
<td>insoluble</td>
<td>insoluble</td>
<td>insoluble</td>
</tr>
</tbody>
</table>

3.7 Swelling ratio

The swelling behaviours of the MWNT/chitosan and MWNT/chitosan-crosslinked membranes were calculated using equation 1, and the results are listed in Table 3. The results reveal that the MWNT/chitosan BP membrane had a greater degree of swelling than the MWNT/chitosan-glycerin and MWNT/chitosan-PEGDE BP membranes in Milli-Q water (~7 pH) due to the higher numbers of hydroxyl groups attached to uncrossed chitosan. On the other hand, the swelling results at pH ~7 are consistent with values previously reported for chitosan hydrogels cross-linked at the surface with other crosslinkers, such as glutaraldehyde [44]. At low pH (acetic-acid solutions), the MWNT-chitosan BP membranes dissolved, making it impossible to estimate the swelling behaviours due to their physical instability [45]. However, bonding glycerin or PEGDE onto the MWNT/chitosan BP membranes improved the swelling resistance in water, acetic acid and sodium hydroxide. Therefore, the MWNT/chitosan-glycerin and MWNT/chitosan-PEGDE BP membranes are stable in acidic and basic solutions and do not swell to the same extent as the MWNT/chitosan BP membrane in aqueous solution. The swelling of chitosan is caused by the electrostatic repulsion between chitosan chains [46]. Tanabe et al. [47] reported that the swelling of chitosan composite membranes can be decreased by preventing the movement of chitosan chains, suggesting that the observed decrease in swelling could be attributed to the hydrogen bonding between glycerin and chitosan that limits chitosan chain movement.
Table 3. Comparison of the swelling behavior and thickness of MWNT-chitosan and MWNT-chitosan-crosslinked: the swelling behaviours of the three BP membranes were measured in 1–5% (v/v) each of acetic acid, Milli-Q water and 3-M sodium hydroxide by adding three small pieces (1 cm × 1 cm) of BP membrane to each solution for 24 h at 21°C.

<table>
<thead>
<tr>
<th>BP membrane</th>
<th>Milli-Q water</th>
<th>Acetic acid 1% (v/v)</th>
<th>Acetic acid 3% (v/v)</th>
<th>Acetic acid 5% (v/v)</th>
<th>NaOH 3 M</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/chitosan</td>
<td>331 ± 15</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>196 ± 11</td>
<td>52 ± 3</td>
</tr>
<tr>
<td>MWNT/chitosan-glycerin</td>
<td>34 ± 5</td>
<td>45 ± 6</td>
<td>83 ± 10</td>
<td>88 ± 8</td>
<td>54 ± 2</td>
<td>52 ± 6</td>
</tr>
<tr>
<td>MWNT/chitosan-PEGDE</td>
<td>52 ± 3</td>
<td>82 ± 9</td>
<td>104 ± 10</td>
<td>105 ± 10</td>
<td>52 ± 6</td>
<td>58 ± 4</td>
</tr>
</tbody>
</table>

3.8 Surface areas and pore structures of membranes

Nitrogen adsorption/desorption isotherms were obtained at 77 K to further investigate the interbundle and intrabundle pore structures and surfaces of the three BP membranes. Nitrogen adsorption/desorption isotherms also allowed the evaluation of the specific surface areas of the BPs, as well as the average pore diameter. Typical isotherms obtained from these membranes are shown in Fig 6, and various data derived from the isotherms are presented in

Table 4. Results in Table 4 show that the specific surface areas of three BPs membranes (MWNT/chitosan, MWNT/chitosan-glycerin and MWNT/chitosan-PEGDE) were significantly lower than those determined in previous studies of BP membranes prepared using MWNTs and MWNTs with other dispersants ([16, 38, 48]). The variations in nitrogen adsorption/desorption at $P/P_o < 0.1$ are likely related to the presence of pores with diameters < 2 nm.
Fig 6. Adsorption isotherm demonstrates a comparative plot of the $P/P_o$ and adsorption of all BP membranes fabricated using a filtration method.

Table 4. The surface areas ($A_{BET}$), average pore diameters ($d_{BET}$), average interbundle pore volume ($D_{bun}$) and water permeability of MWNT/chitosan, MWNT/chitosan-glycerine and MWNT/chitosan-PEGDE BP membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>$A_{BET}$ BP membrane (m$^2$/g)</th>
<th>Pore diameter (nm)</th>
<th>Interbundle pore volume (%)</th>
<th>Water permeability (L m$^{-2}$ h$^{-1}$ bar$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/Trix $^a$</td>
<td>300 ± 1.0</td>
<td>24 ± 1</td>
<td>91 ± 5</td>
<td>24 ± 6</td>
</tr>
<tr>
<td>MWNT/C6S $^c$</td>
<td>250 ± 1.0</td>
<td>26 ± 3</td>
<td>94 ± 6</td>
<td>17 ± 4</td>
</tr>
<tr>
<td>MWNT/PTS $^c$</td>
<td>180 ± 0.1</td>
<td>20 ± 2</td>
<td>96 ± 8</td>
<td>23 ± 6</td>
</tr>
<tr>
<td>MWNT/TSP $^c$</td>
<td>240 ± 1.0</td>
<td>26 ± 3</td>
<td>92 ± 5</td>
<td>21 ± 3</td>
</tr>
<tr>
<td>MWNT/chitosan</td>
<td>11 ± 2</td>
<td>3.7 ± 0.1</td>
<td>67 ± 4</td>
<td>0.87 ± 0.03</td>
</tr>
<tr>
<td>MWNT/chitosan-glycerin</td>
<td>1 ± 0.2</td>
<td>2.5 ± 0.1</td>
<td>13 ± 1</td>
<td>0.61 ± 0.02</td>
</tr>
<tr>
<td>MWNT/chitosan-PEGDE</td>
<td>0.07 ± 0.01</td>
<td>2.1 ± 0.1</td>
<td>*</td>
<td>0.19 ± 0.01</td>
</tr>
</tbody>
</table>

*Unable to estimate. $^a$ Data for MWNT/Trix taken from reference[16]. $^c$ Data for MWNT/C6S, MWNT/PTS and MWNT/TSP taken from reference[38].
Each isotherm in Fig 6 was used to calculate pore-size distribution using the BJH and HK methods [31, 32]. The HK method provides information relative to the distribution of small pores (i.e. <2 nm), whereas the BJH method can assess relatively the distribution of the large pores of all BP membranes. Results were obtained for pore-size distribution of each BP membrane (Fig 7) by combining the data from these two methods. The large peak from 0.5–1 nm is related to the pores between MWNT (intrabundle). However, variation >1 nm appeared in the distributions of the large pores. These interbundle pores are shown in the SEM images (Fig 4A–C) [49]. Numerical integration of the curves of Fig 7A–C reveal that these larger interbundle pores are responsible for 67% of the total free volume of MWNT/chitosan and only 13% of MWNT/chitosan-glycerin. The interbundle pore volume percentages for the three BP membranes are very small compared to the values of the results for the MWNT-Trix, MWNT-C6S, MWNT-PTS and MWNT-TSP, BP membranes as shown in Table 4 [16, 38]. In addition, the MWNT BPs investigated in this work have much narrower internal pores separating aggregates of MWNT with a small average diameter. This accounts for why the interbundle pore volumes determined for the MWNT BP membranes (range 13–67%) are much lower than what was measured previously for the BP membranes composed of SWNTs (range 76-93%) [15]. Data of the pore structure information resulted through analysis of nitrogen adsorption/desorption isotherm therefore exposed that there are generally some significant differences for BP membranes fabricated using the different classes of CNTs and dispersants. Therefore, the results in this work indicate that it may be possible to control the porosity of BP membranes by using MWNT with chitosan and chitosan-crosslinked to be useful for desalination area.
Fig 7. Pore-size distributions for BP membranes were determined using the HK (blue peak) and BJH methods (orange dotted peak), which were obtained from nitrogen adsorption/desorption isotherms: A) MWNT/chitosan; B) MWNT/chitosan-glycerin; and C) MWNT/chitosan-PEGDE; all BP membranes were prepared using a filtration method.

3.9 Zeta potential

Membrane-surface charge density can be determined by measuring the membrane surface ZP. Techniques to estimate the ZP have been described in detail by Childress and Elimelech [50]. The ZPs of the three investigated BP membranes were determined by the method described previously in the experimental section. The results are plotted as a function of pH in Fig 8. All three BP membranes were neutral between pH 4 to 8. They were slightly positive at below pH 4 and slightly negative at above pH 8. Results in Fig 8 are consistent with the fact that MWNTs do not have any ionisable functional groups. The slightly positive and negative charge at below pH 4 and above pH 8 respectively are possibly due to the protonation and deprotonation of the dispersant (i.e. chitosan,
chitosan-glycerin, and chitosan-PEGDE) residuals in the membrane matrix [50, 52]. Our results are also consistent with a previous study Rashid [51], which showed the isoelectric point of the MWNT/Chitosan at near neutral pH (i.e. 8.6). The membrane prepared by Rashid was slightly positively charged and negatively charged at below and above this isoelectric point of pH 8.6. Zhan et al [35] prepared CNT–CS BP membranes using a similar approach and reported the isoelectric point of their membranes at pH 5.3, which is within the range of pH 4 to 8 reported in our study.

![Fig 8. ZPs of the three BP membranes as a function of pH.](image)

**3.10 Water permeability**

Water permeability was determined for the large BP membranes (40 cm²) using the procedure outlined in the experimental section, wherein the permeate flux was plotted against applied pressure to force the liquid through the membrane. Results are plotted in Fig 9, and water permeability was calculated from the slopes of the liner relationship between permeate flux and applied pressure.
Fig 9. Permeate flux as a function of applied pressure of three BP membranes; the resulting straight lines represent a linear fit to the experimental data obtained.

The permeate fluxes of all BP membranes (i.e. MWNT/chitosan and MWNT/chitosan-crosslinked) increased with greater applied pressure [15]; results are presented in Table 4. After 8 h of operation for each BP membrane, the MWNT/chitosan BP membrane exhibited an average water-permeability rate of approximately $0.867 \pm 0.03$ L m$^{-2}$ h$^{-1}$ bar. This was 1.3 times higher than the average water-permeability rate ($0.605 \pm 0.02$ L m$^{-2}$ h$^{-1}$ bar$^{-1}$) of the MWNT/chitosan-glycerin, and 4.4 times greater than the average water-permeability rate ($0.189 \pm 0.1$ L m$^{-2}$ h$^{-1}$ bar$^{-1}$) of the MWNT/chitosan-PEGDE. In particular, the water permeability obtained with the MWNT/chitosan-PEGDE BP membrane was significantly lower (approximately a 78% decrease in flux during an 8h filtration experiment) than that obtained with the MWNT/chitosan membrane. Many studies have reported that the crosslinking (crosslinking agent) of chitosan membranes caused reductions in pore size and water permeability [53-55]. The water permeability results for three BPs in this work are agreed well with those results reported for the surface and pore size as shown in
Therefore, the MWNT/chitosan-crosslinked (MWNT/chitosan-PEGDE) can cause a reduction in membrane permeability when filtering pure water.

### 3.11 Salt-rejection capability

Salt rejection by the three BP membranes (MWNT/chitosan, MWNT/chitosan-glycerin and MWNT/chitosan-PEGDE) was determined using a crossflow RO/NF system as shown in Fig. 1 with four inorganic electrolytic solutions NaCl, MgCl$_2$, MgSO$_4$ and Na$_2$SO$_4$ (experiments were carried out as a single salt solution) having salt concentrations of 2 g/L and applied different pressures at a temperature of 20 ± 2 °C for 8 h. Rejection of each salt by the MWNT/chitosan, MWNT/chitosan-glycerin and MWNT/chitosan-PEGDE membranes (as described by equation 2 in the experimental section) were plotted against permeate flux (Fig 10).

Overall, salt rejection increased as the permeate flux increased. NaCl rejection by the MWNT/chitosan-PEGDE membrane was the highest (46-63%) among all three membranes investigated here. This value was approximately, three times higher than the average NaCl rejection by the MWNT/chitosan membrane (approximately 21%) and two time higher than the average NaCl rejection of MWNT/chitosan-Glycerin (approximately 19-38%). These results are consistent to the measured pore size of the investigated BP membranes (Table 4) where the MWNT/chitosan-PEGDE membrane showed the smallest pore size. A similar rejection data for NaCl using different type of NF membranes were obtained elsewhere [28]. Moreover, the MWNT/chitosan-PEGDE membrane also had a greater rejection for MgSO$_4$ (approximately 33-37%) than that of the MWNT/chitosan (18-23%) and MWNT/chitosan-glycerin membranes (17-23%). It is noted that Na$_2$SO$_4$ rejection by these three BP membranes were quite low (Fig 10). Na$_2$SO$_4$ rejection by the MWNT/chitosan was 6-9%.
The observed low rejections of divalent salts (e.g. MgSO₄ and Na₂SO₄) could be explained by the lack of any surface charge of these BP membranes (section 3.9). It is most notable that salt rejection in this research (Fig 10) follows the order of R(MgCl₂) > R(NaCl) > R(MgSO₄) > R(Na₂SO₄) for three BP membranes under the same operating conditions. These results are in contrast to the rejection behavior of the conventional polyamide NF membranes, in which the rejection of divalent salts is usually higher than that of monovalent salts [53, 56]. It is noteworthy that the conventional polyamide membranes are significantly negatively charged at around pH 7 and thus electrostatic
interaction can play a major role in the rejection of cations and anions. By contrast, the MWNT BP membranes in this study were neutral at pH 7, thus, electrostatic interaction is not expected as a major rejection mechanism. Of a particular note, the order of rejection reported here coincides with the decreasing order of unhydrated ionic radius of Cl$^-$(0.19 nm) > Na$^+$(0.1 nm) > Mg$^{2+}$ (0.09 nm) Kielland [57]. The unhydrated ionic radius of SO$_4^{2-}$ is not available in the literature. The three BP membranes have neutral surface charge at pH 7, which can explain for a higher rejection of mono-valent ions (e.g. Cl$^-$) than for multi-valent ions (e.g. SO$_4^{2-}$) for the size effect. Our results are consistent with a previous study by Tongwen et al [58] who also showed that the rejection of various inorganic electrolytes were in the order of $R$(MgCl$_2$) > $R$(NaCl) > $R$(MgSO$_4$). Similar to our work, the membrane investigated by Tongwen et al., [58] was not negatively charged. The separation of MgCl$_2$ could be higher than that of Na$_2$SO$_4$ and NaCl, as was also found by Rios et al. [59] in their study of a positively charged membrane. Therefore, the membrane charge determines the dependence of the separation on the electrolyte valence type, on the rejection of salt by the three charged BP membranes, which occur predominantly through surface interaction between the membrane and ions.

Furthermore, the rejection of NaCl by MWNT/chitosan and MWNT/chitosan-cross-linked BP membranes was studied at $20 \pm 2$ °C at the pH range from 3 to 10. The transmembrane pressure was adjusted to obtain the same permeate flux for studying the effect of pH on the salt rejection as presented in Fig 11. All the membranes (MWNT/chitosan and MWNT/chitosan-crosslinked) had increased salt (NaCl) rejection when the feed solution pH became acidic. The increase in the NaCl rejection by all three BP membranes when subjected to lower pH may be attributed to the protonation of free amino groups in chitosan. Previous studies have described that –NH$_2$ on chitosan can be protonated at low pH. As a result, the NH$_3^+$ group on the chitosan can play an important role because the group is chiefly responsible for interactions with anions and negatively charged surfaces [60, 61]. Moreover, Fig 11 also demonstrates that the MWNT/chitosan-PEGDE membrane had a greater rejection for NaCl than the MWNT/chitosan and MWNT/chitosan-glycerin membranes. This may be attributed to the charge repulsion, which can result in higher rejection based on steric interactions. It is likely that the evidence would be much clearer if smaller ions were selected.
4. CONCLUSIONS

Three buckypaper (BP) membranes for nanofiltration application were fabricated from composting multi-walled carbon nanotubes (MWNT) with chitosan containing quaternary amine groups (chitosan and chitosan-crosslinked by in situ amine crosslinking). A comprehensive study for properties of these membranes was investigated. The chitosan, chitosan-glycerin and chitosan-PEGDE as dispersants offered a pathway for enhancing the dispersal of MWNTs in water. In addition, they provided an excellent conductivity range (60–70 S/cm), and an extremely high tensile strength compared to the BPs prepared by the vacuum-filtration method using MWNTs and various dispersants, such as Trix, cipro and τ-carrageenan. Contact angle studies for three BP membranes indicated that the crosslinked of chitosan to the glycerin and PEGDE made the surface of membranes more hydrophilic and stable in different solutions. Further, the permeate flux sequence of BP membranes is MWNT/chitosan > MWNT/chitosan-glycerin > MWNT/chitosan-PEGDE. The MWNT/chitosan BP membrane provides more accessible free volume for water transport than the MWNT/chitosan-PEGDE and MWNT/chitosan-glycerin content. Salt rejection of three BP membranes follows the order of $R(\text{MgCl}_2) > R(\text{NaCl}) > R(\text{MgSO}_4) > R(\text{Na}_2\text{SO}_4)$.
under the same operating conditions. These results indicate that the separation of these inorganic cations and anions are mostly governed by the size of their unhydrated radius.

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REFERENCES


[37] K. Dusek, Phase separation during the formation of three-dimensional polymers, 16 (1967) 1289-1299.


