The Effect of PCA-g-MWCNTs Loading on the Performance of PES/MWCNTs Hemodialysis Membrane

Muhammad Nidzhom Zainol Abidin\textsuperscript{a}, Pei Sean Goh\textsuperscript{*,a}, Ahmad Fauzi Ismail\textsuperscript{a}, Mohd Hafiz Dzarfan Othman\textsuperscript{a}, Hasrinah Hasbullah\textsuperscript{a}, Noresah Said\textsuperscript{a}, Siti Hamimah Sheikh Abdul Kadir\textsuperscript{b}, Fatmawati Kamal\textsuperscript{b}, Mohd Sohaimi Abdullah\textsuperscript{a}, Be Cheer Ng\textsuperscript{a}

\textsuperscript{a}Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 Skudai, Johor Darul Ta'zim, Malaysia

\textsuperscript{b}Institute of Molecular Medicine and Biotechnology, Faculty of Medicine, Universiti Teknologi MARA Sungai Buloh Campus, Jalan Hospital, 47000 Sungai Buloh, Selangor, Malaysia

\textsuperscript{*}peisean@petroleum.utm.my

Membrane fouling is one of the biggest obstacles towards hemodialysis treatment. In this work, multi-walled carbon nanotubes (MWCNTs) are incorporated to enhance the hydrophilicity and antifouling property of polyethersulfone (PES) hemodialysis membrane. Prior to the mixing, surface functionalisation of MWCNTs was carried out to introduce a large hyperbranched poly (citric acid) (PCA) for better dispersion. PCA-grafted (g)-MWCNTs were prepared by grafting citric acid monohydrate onto the wall of purified MWCNTs. PCA-g-MWCNTs (0 - 0.2 wt\%) were then dispersed in PES and polyvinylpyrrolidone blends. The membranes were spun at 50 cm air gap, characterised in terms of morphology and hydrophilic properties before tested for pure water flux (PWF) and protein rejection using bovine serum albumin (BSA). The results revealed that, compared to the neat PES membrane, the PES/MWCNTs membranes were more hydrophilic. The highest PWF (110.4 L m\textsuperscript{-2} h\textsuperscript{-1}) was achieved by the membrane incorporated with 0.1 wt\% PCA-g-MWCNTs. Same trend was observed for protein rejection, where up to 0.1 wt\% loading of PCA-g-MWCNTs, the PES/MWCNTs membrane rejected 97.3 \% of BSA compared to 88.2 \% as obtained from the neat membrane. It was found that the PES/MWCNTs membranes possessed a greater PWF recovery ratio, proving that the membranes antifouling property was improved. The addition of PCA-g-MWCNTs in the membranes enhanced the hydrophilicity as well as the antifouling property of the PES membrane for hemodialysis application.

1. Introduction

Hemodialysis becomes one of the emerging applications that utilises membrane separation process. Hemodialysis is just the same as any other pressure-driven membrane processes. The core difference between them is that hemodialysis requires a far lower operating pressure (< 0.5 bar) to prevent from damaging the blood capillaries. A hemodialysis membrane must be able to remove body wastes and supply essential nutrients into blood (Zhang et al., 2014). To allow rapid separation while keeping low pressure require membranes with smaller dimension to ease the transport of molecules. The challenges derived from this include the way to maintain the membrane sustainability and performance with a long, repeated treatment. This is because a smaller membrane might welcome unwanted solutes due to the larger surface area in contact with blood. The rising demand for a more sustainable dialyser has stimulated the fabrication of durable membrane with less fouling (Stoller, 2015). In the past 15 years, synthetic polymers like polyethersulfone (PES), for example, have been chosen due to their outstanding oxidative, thermal, chemical, and mechanical stability (Zhao et al., 2012). Despite that, flux and separation performance decline remains as the drawback of using this hydrophobic polymer due to fouling (Su et al., 2011). Low pure water flux (PWF) was proven to render low removal of middle molecular uremic toxins. The decrease in protein rejection is also caused by the hydrophobic interactions between proteins and the membrane surface.

Please cite this article as: Abidin M.N.Z., Goh P.S., Ismail M.H.D., Hasbullah H., Said N., Kadir S.H.S.A., Kamal F., Abdullah M.S., Ng B.C., 2017, The effect of pca-g-mwcnts loading on the performance of pes/mwcnts hemodialysis membrane, Chemical Engineering Transactions, 56, 1609-1614 DOI:10.3303/CET1756269
Modification of PES membrane was done to allow better hydrophilicity (Huang et al., 2012), where it has a positive effect on flux, separation and antifouling performance (Zhao et al., 2012). Inorganic nanofiller was previously embedded into the host material (Favvas et al., 2014) to tailor the physical and chemical properties of the membrane. Carbon nanotube (CNT) has been proven to perform outstandingly in wastewater separation from biological water pollutants (Das et al., 2014). CNTs are prominent additives in polymer-based composites due to their nanoscale dimension, chemical inertness, large surface area, and high strength (Zhang et al., 2014). To enhance membrane hydrophilicity, CNTs are functionalised with hydrophilic polymers by chemical grafting approach to form CNT-polymer nanocomposites (Adeli, 2008). Attempt has been made previously to functionalise multi-walled carbon nanotubes (MWCNTs) with poly (citric acid) (PCA), a biocompatible and water-soluble polymer (Adeli et al., 2014) to form PCA-grafted (g)-MWCNTs (Abidin et al., 2016). The effect of PCA-g-MWCNTs addition on the membrane separation and antifouling performance was studied. Compared to oxidised MWCNTs, PCA-g-MWCNTs provided better antifouling properties for the membrane. The aim is to investigate in detail the relationship between the MWCNTs loading and the separation features of the membrane as well as the antifouling performance. A systematic study of different concentrations of MWCNTs incorporated in the membrane is imperative to select the right proportion for optimal performance.

2. Experimental

2.1 Materials

PES (Radel A-300A Resin) was purchased from Solvay Advanced Polymers; pristine MWCNTs (> 98 % carbon basis, outer diameter: 6 - 13 nm, length: 2.5 - 20 µm), PVP (molecular weight = 360,000 g/mol) and bovine serum albumin (BSA) of > 98 % purity were obtained from Sigma Aldrich; N-methyl-2-pyrrolidone (NMP, 99.5 %; molecular weight = 99.1 g/mol) was purchased from Acros Organics; citric acid monohydrate (C_6H_8O_7.H_2O; molecular weight = 210.15 g/mol), cyclohexane and tetrahydrofuran (THF) were purchased from Fisher Scientific; sulfuric acid (95 - 97 %) and nitric acid (65 %) were obtained from Merck Millipore.

2.2 Synthesis of PCA-g-MWCNTs

Pristine MWCNTs (2 g) were purified using acid mixture (4 M sulfuric acid and 4 M nitric acid in the ratio of 3 : 1). The oxidation process was performed at 110 °C for 24 h. The oxidised (O)-MWCNTs were washed repeatedly with distilled water until the pH of the filtrate approaches neutral value. The collected O-MWCNTs were then dried for 24 h at 50 °C in oven. O-MWCNTs was further functionalised with citric acid monohydrate via melting esterification and polycondensation as reported in literature (Abidin et al., 2016) to form PCA-g-MWCNTs.

2.3 Preparation of PES/MWCNTs Membranes

Table 1 shows the dope solution compositions. The hollow fibre membrane was spun using a spinneret with the dimension of 0.6 / 0.3 mm for outer and inner diameters. Distilled water was used as the bore fluid while tap water was chosen as the coagulation bath. The spinning parameters used were listed in Table 2. The fabricated membrane was immersed in tap water for 3 d. Next, the membrane was kept in 50 wt% glycerol for 1 d before drying.

Table 1: Composition of polymer solutions for respective membranes (wt%)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>PES</th>
<th>PVP</th>
<th>Water</th>
<th>NMP</th>
<th>PCA-g-MWCNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>M0</td>
<td>17.6</td>
<td>4.8</td>
<td>3.0</td>
<td>74.6</td>
<td>-</td>
</tr>
<tr>
<td>M0.05</td>
<td>17.6</td>
<td>4.8</td>
<td>3.0</td>
<td>74.55</td>
<td>0.05</td>
</tr>
<tr>
<td>M0.1</td>
<td>17.6</td>
<td>4.8</td>
<td>3.0</td>
<td>74.5</td>
<td>0.1</td>
</tr>
<tr>
<td>M0.2</td>
<td>17.6</td>
<td>4.8</td>
<td>3.0</td>
<td>74.4</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 2: Spinning parameter for hollow fibre spinning process

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air gap (cm)</td>
<td>50</td>
</tr>
<tr>
<td>Dope extrusion rate (mL/min)</td>
<td>1</td>
</tr>
<tr>
<td>Collection speed (m/min)</td>
<td>10</td>
</tr>
<tr>
<td>Bore fluid flow rate (mL/min)</td>
<td>1</td>
</tr>
</tbody>
</table>
2.4 Membrane characterisations
2.4.1. Scanning electron microscopy (SEM)

The morphology of PES/MWCNTs membranes was examined using SEM. The images of cross-sections and outer surfaces of the membranes were collected.

2.4.2. Porosity

Dry-wet weight method was used to measure membrane porosity, $\varepsilon$. The membrane was immersed in pure water for 1 h to achieve equilibrium before measuring its weight. The porosity of membrane was defined in Eq(1).

$$\varepsilon = \frac{w_1 - w_2}{V \rho_w} \times 100\%$$

where $\varepsilon$ is the membrane porosity (%), $w_1$ is the mass of the wet membrane, $w_2$ is the mass of the dry membrane, $V$ is the membrane volume and $\rho_w$ is the water density (1.0 g/cm$^3$).

2.5 Water contact angle

The hydrophilic property of membranes was measured using contact angle goniometer (Krüss Gambult, Germany). 0.2 µL of water was dropped on the membrane surface and the contact angle was measured.

2.6 Evaluation of membrane separation performance

The PWF, $J$ and BSA rejection, $R$ of the membranes were measured to evaluate the membranes separation performance. The membrane PWF was calculated using the Eq(2):

$$J = \frac{V}{A \Delta t}$$

where $J$ represents the PWF (L m$^{-2}$ h$^{-1}$), $V$ is the volume of permeate (L), $A$ is the total surface area (m$^2$) while $\Delta t$ is the permeation time (h). For protein rejection test, 500 ppm BSA solution was used. The percent rejection was calculated by Eq(3).

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

where $C_p$ and $C_f$ are the BSA concentrations of the permeate and feed. The concentration of BSA was measured using UV-Vis Spectrophotometer (DR 5000). After the completion of protein rejection experiment, each membrane was cleaned by immersing the membrane in a beaker of deionised water, ultrasonicated for 15 min. Subsequently, a new set of PWF was measured again.

3. Results and discussion

3.1 Viscosity of PES/MWCNTs dope solutions

The rheological property of dope solutions was determined by measuring viscosity. As shown in Table 3, the increasing amount of MWCNTs increased the viscosity of the dope solutions. Higher viscosity is due to the decrease in shear rate (Zhang et al., 2014). The addition of more MWCNTs strongly restrained the shear flow between PES chains and PVP, resulted in the increase of viscosity.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Viscosity (mPa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M0</td>
<td>5,121</td>
</tr>
<tr>
<td>M0.05</td>
<td>6,564</td>
</tr>
<tr>
<td>M0.1</td>
<td>7,982</td>
</tr>
<tr>
<td>M0.2</td>
<td>9,044</td>
</tr>
</tbody>
</table>

3.2 Morphologies of PES/MWCNTs membranes

Based on Figure 1, as the amount of MWCNTs increases, the finger-like structures became longer as the result of faster phase inversion. The formation of long and larger voids would lead to better PWF (Bouré and Vanholder, 2004). Besides, the membranes maintained the trend of increasing pore size at the sublayer up to 0.1 wt% MWCNTs loading (Figure 2). This happened due to the influence of high dope solution viscosity on the moisture-induced phase inversion, which is taking place slowly at the outer side of the nascent hollow fibre.
Beyond the loading (0.2 wt%), the stronger force exerted from the inner side of the membrane has affected the molecular orientation and reduce membrane free volume. With regards to the reducing pore size (Figure 2(d)), the more viscous dope solution has suppressed the pore formation despite experiencing a delayed phase separation at the outer surface.

Figure 1: Cross-sectional images of membrane (a) M0 (b) M0.05 (c) M0.1 and (d) M0.2

Figure 2: Surface images of membrane (a) M0 (b) M0.05 (c) M0.1 and (d) M0.2

3.3 Separation features of PES/MWCNTs membranes

As tabulated in Table 4, the results showed the improvement of membranes hydrophilicity as the increasing amount of MWCNTs. The same trend was also observed on the membranes porosity (Table 4). However, it was found that the porosity of membrane M0.2 has declined. The high dope solution viscosity and saturation of MWCNTs became the two elements suspected to render the decline in porosity. The viscosity of the dope solution has reached the level where it delayed the phase separation, leading to the formation of a denser structure in the membrane sublayer (Celik et al., 2011). The addition of too much MWCNTs especially for a small-sized fibre easily caused MWNCTs saturation in the polymer matrix. This resulted in the formation of agglomerates which reduced the free space between the nanotubes. The improvement in PWF especially at
0.05 wt% and 0.1 wt% MWCNTs could be attributed to the enhanced surface hydrophilicity of the membranes. The highly hydrophilic PCA-g-MWCNTs facilitated their dispersion in the PES matrix, which improved the membrane performance (Ismail et al., 2011). The larger pores induced the water transport properties of the membranes. In terms of separation quality, all membranes except membrane M0 reached the minimum benchmark of sufficient protein rejection set for a hemodialysis membrane (90%). The main reason was due to the compact arrangement of nano-sized pores at the skin layer. Both PWF and BSA rejection undesirably decreased when the loading of MWCNT was further increased beyond 0.1%. The smaller pore size and lower porosity of membrane M0.2 were known to cause the decrease in PWF (Sianipar et al., 2015). In the case of lower BSA rejection for the membrane M0.2, it could be attributed to the agglomeration of MWCNTs. The formation of clusters due to the electrostatic interactions of MWCNTs-MWCNTs and PES-MWCNTs has led to irregularities in the polymer matrix and on the surface (Sianipar et al., 2015), exposing the hydrophobic sites which permitted more BSA molecules to pass through the membrane. Hence, the rejection performance was deteriorated.

Table 4: Results of contact angle, porosity, PWF and BSA rejection of PES/MWCNTs membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Contact angle (°)</th>
<th>Porosity (%)</th>
<th>J (L m⁻² h⁻¹)</th>
<th>R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M0</td>
<td>77.6</td>
<td>41.3</td>
<td>16.1</td>
<td>88.2</td>
</tr>
<tr>
<td>M0.05</td>
<td>56.1</td>
<td>75.7</td>
<td>95.2</td>
<td>94.9</td>
</tr>
<tr>
<td>M0.1</td>
<td>51.6</td>
<td>76.9</td>
<td>110.4</td>
<td>97.3</td>
</tr>
<tr>
<td>M0.2</td>
<td>48.1</td>
<td>73.6</td>
<td>56.8</td>
<td>93.7</td>
</tr>
</tbody>
</table>

3.4 Antifouling performance of PES/MWCNTs membranes

The membrane antifouling property was determined in terms of PWF recovery ratio, which is becoming an important criterion in the hemodialysis application (Irfan and Idris, 2015). From the data gathered from the membrane flux behaviour (Figure 3(a)), all membranes incorporated with PCA-g-MWCNTs took around 100 min to obtain the steady flux which is longer than the time taken by the neat PES membrane, showing less tendency to foul. The result of membranes PWF recovery ratio, as shown in Figure 3(b) indicated that the antifouling ability of membranes incorporated with more PCA-g-MWCNTs was considerably improved. Owing the PWF recovery ratio of 81%, membrane M0.1 shows the best antifouling performance. The synergism between the high surface area MWCNTs and highly hydrophilic PCA brushes has induced the formation of a denser and more stable pure water (Zhang et al., 2013) to barricade the membrane pores from foulants. As the result, the membrane PWF recovery ratio was improved.

Figure 3: (a) Flux behavior of the PES/MWCNTs membranes at: 60 min of pure water filtration (t = 0 - 60 min), 120 min of BSA solution (500 ppm) filtration (t = 60 - 180 min), and 60 min of pure water filtration after cleaning process (t = 180 - 240 min) (b) the PWF recovery ratio of the membranes
4. Conclusions

In conclusion, all membranes possessed an asymmetrical morphology with inner selective skin layer, compact spongy sub-layer and finger-like macro-voids. As the MWCNTs loading is increased, the finger-like voids become longer and closely arranged to each other. At the membrane outer surface, the pore size kept increasing until at 0.1 wt% of MWCNTs loading. The optimum MWCNTs loading for the membrane was determined to be 0.1 wt% in which this membrane exhibited PWF and BSA rejection of 110.4 L m$^{-2}$ h$^{-1}$ and 97.3 %. It was also found that the most promising antifouling properties was bestowed on the membrane based on the flux decline behaviour and enhanced PWF recovery ratio (81 %).

Acknowledgments

We gratefully acknowledge the financial support from the Universiti Teknologi Malaysia and Ministry of Higher Education Malaysia (Grant no: 01G46).

Reference


Adeli M., 2008, Carbon nanotube-graft-poly (citric acid) nanocomposites, NANO 3 (1), 37-44.


Stoller M., 2015, About the development of advanced membrane process control systems, Chemical Engineering Transactions 43, 1393-1398.


