1. Introduction

PVDF is among attractive materials in membrane fabrication. PVDF possesses high thermal stability, good chemical resistance and resistance to many corrosive materials. These properties have made PVDF popular in many membrane applications such as membrane distillation, membrane contactors, water/organic separation and ultrafiltration [1–6]. Despite of its popularity, PVDF membranes are still suffering from one major drawback, which is fouling, during microfiltration or ultrafiltration of aqueous solutions. The natural hydrophobic properties of PVDF membranes make it easily susceptible to fouling, which may lead to a serious flux decline during long-term operations. Proteins that present in the solution feed may be adsorbed onto membrane surfaces or onto the membrane’s pore walls, causing a decrease in permeate flux, consequently affecting the efficiency of the overall processes.

Many techniques have been explored to improve the hydrophilicity of PVDF membranes. These include coating of hydrophilic polymer/materials onto membrane surfaces [7,8], surface grafting by high energy electron beam or plasma treatment [9–11], and blending of hydrophilic materials, such as amphiphilic copolymers in a membrane solution [12–14]. However, the coated layer has limitations in terms of long term stability, where the layer could be removed during cleaning or long-term operation, while surface grafting requires additional steps and costs for employing plasma or electron beam. Compared to these techniques, the blending of amphiphilic copolymers appears to be one of the practical methods in the industrial scale applications because it can be considered as a single-step method for preparing hydrophilic membranes using hydrophobic membrane materials, and at the same time it can retain the membrane hydrophilicity. Amphiphilic copolymers are self-organising blends of hydrophobic and hydrophilic polymers, which are designed such that the hydrophobic backbone provides compatibility with the matrix material and water insolubility, while the hydrophilic side chains present the desired surface hydrophilicity.

There have been several studies that report the preparation of hydrophilic PVDF membranes by blending the amphiphilic
copolymer with the polymer or membrane solution [12–15]. In most cases, the preparations involve the formation of hydrophilic flat sheet PVDF membranes, rather than hollow fibre membranes. Geometrically, the hollow fibre configuration is preferred over the flat sheet owing to its high surface area per unit volume, which is one of the crucial aspects in industrial membrane productions. The hollow fibres can be easily scaled up and provide easy maintenance through the use of hollow fibre cartridges. However, the fabrication of hollow fibre membranes is universally recognised to be much more complicated than that of flat sheet membranes. This is because the formation of hollow fibre membranes depends on spinning parameters, which are considerably more complex compared to the casting parameters of flat sheet membranes. Although considerable effort is being devoted to the fabrication of PVDF hollow fibre membranes with the desired properties [16–21], but to our best knowledge, there has been only a single study that report the fabrication of the hydrophilic PVDF membrane from amphiphilic polymer in hollow fibre configuration [22]. Besides, this study is mainly focused on the conventional or direct method of surface modification of PVDF membranes from amphiphilic copolymer.

In this work, we aim to modify the PVDF polymer solution via in-situ grafting of PVDF-g-polyethylene glycol methyl ether methacrylate (PEGMA), which eventually will lead to the formation of hydrophilic PVDF hollow fibre membranes. Hollow fibre spinning solutions are prepared, which undergo a chemical reaction through atom transfer radical polymerisation (ATRP) to produce PVDF-g-PEGMA copolymer. The solution is suitable for spinning because of several reasons [23]: (a) 1-methyl-2-pyrrolidone (NMP) solvent can also be used to dissolve PVDF, instead of using dimethylacetamide (DMAc), (b) The amounts of copper (I) chloride (CuCl) and ligand 4,4'-dimethyl-2,2'-dipyridyl (DMDP) present in the bulk polymerisation solution are relatively small, (c) some of the CuCl have been converted to copper (II) chloride (CuCl₂) that is a water-soluble salt, and (d) the excess or unreacted PEGMA can act as a pore forming agent. Further objectives are to investigate the effects of a copolymer addition on the solution’s viscosity, effects of air gap distance, copolymer concentration, ethanol addition and dope extrusion rate on the ultimate membrane morphology and performance.

2. Experimental

2.1. Materials

Commercially available poly(vinylidene fluoride) (PVDF, Kynar® 761) powder was obtained from Atofina Chemicals Inc., USA. Poly(ethylene glycol) methyl ether methacrylate (PEGMA, \(M_n=475\) g/mol), copper (I) chloride (CuCl), 4,4'-dimethyl-2,2'-dipyridyl (DMDP), silicone oil, a mixture of different dextran molecular weights (10,000–150,000 Da), bovine serum albumin (BSA, Fraction V) and phosphate-buffered saline (PBS) were purchased from Sigma Aldrich, UK. 1-methyl-2-pyrrolidone (NMP) was purchased from Rathburn Chemicals Ltd, UK. All solvents and chemicals were reagent grade, and all reagents were

<table>
<thead>
<tr>
<th>Hollow fibre</th>
<th>Composition</th>
<th>Spinning parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PVDF (%)</td>
<td>Copolymer (%)*</td>
</tr>
<tr>
<td>Pure PVDF-30</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>Pure PVDF-0</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>F1-30</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>F1-0</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>F2-30</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>F2-0</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>F3-30</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>F3-0</td>
<td>20</td>
<td>3</td>
</tr>
</tbody>
</table>

Fig. 1. FTIR-ATR spectra for I-(a) pure PVDF membrane, I-(b) F1-30, I-(c) F1-0, I-(d) F2-30, I-(e) F2-0, I-(f) F3-30, I-(g) F3-0 and II PEGMA.
used as received. The PBS solution \((\text{pH} = 7.4)\) was prepared by the addition of pre-packaged buffered salts to deionised water.

2.2. Preparation and spinning of hydrophilic PVDF hollow fibre membrane

Hollow fibre dope solutions were prepared by mixing different amounts of copolymer solution synthesised by the ATRP method \([23]\), with PVDF and NMP. The detailed experimental set-up and spinning procedure has been described elsewhere \([24]\). In this study, the copolymer obtained from polymerisation was in the ratio of 1:10 from the overall amount before polymerisation, thus the percentage of copolymer that contain in dope solution is calculated based on this ratio. PVDF concentrations were kept at 20 wt% throughout the experiments. Prior to spinning, the dope solutions were degassed under vacuum for 1 h to remove the air bubbles. Fibres were extruded through a spinneret with the dimension of outer diameter/inner diameter of 1.0/0.7 mm. In order to study the effects of the extrusion rate on the hollow fibres’ morphology and performance, spinning at different extrusion rates of 1.5, 10 and 20 mL/min was performed. Water has been used as the external coagulant medium throughout the experiment while different compositions of the internal coagulant were used. The dope compositions and spinning conditions for hollow fibres are listed in Table 1. Hollow fibre membranes were immersed into water for 3 day and subjected to daily water changing to remove the residual solvent and unreacted monomer. Prior to membrane characterisation, the hollow fibre membranes were pre-treated with ethanol before drying at room temperature.

2.3. Characterisation of hollow fibre membrane morphology and performance

The presence of PVDF-g-PEGMA in the hollow fibre membranes fabricated via the in-situ grafting of spinning solution was analysed by using Fourier transform infra-red (FTIR) spectrometer (Perkin Elmer, Spectrum One equipped with an attenuated total reflection (ATR) attachment). Also FTIR spectrum for the PEGMA monomer was obtained to be compared with the grafted copolymer on the surface of the hollow fibres. The samples were placed on the sample holder and all spectra were recorded in the wave number range of 4000–500 cm\(^{-1}\) by cumulating 32 scans at a resolution of 2 cm\(^{-1}\).

The morphology of the cross-section and surface of the prepared hollow fibre membranes were examined with Scanning Electron Microscope (SEM; JSM-5610LV, JEOL, Tokyo, Japan) and Field Emission Scanning Electron Microscope (FESEM Leo Gemini 1525). The hollow fibres were immersed in liquid nitrogen for

Fig. 2. SEM cross-sectional images of hollow fibre membranes prepared from 1.5 wt% graft copolymer (PVDF-g-PEGMA) with different air gaps (a) 30 cm air gap, (b) 10 cm air gap and (c) 0 cm air gap.
about 10 min and then fractured into short samples, for the purpose of maintaining the original cross-sectional of the membranes. The samples were then positioned on a metal holder, sputter coated with gold or chromium under vacuum for 3 min. The micrographs of the cross section and surface of the hollow fibre membranes were taken at various magnifications.

Static contact angle measurements on the hollow fibre membranes were conducted using the Drop Shape Analyser (DSA 10 MK2, Krüss GmbH, Hamburg, Germany). The sessile drop study was carried out using deionised water on dry samples. Water contact angles were measured by putting sessile water droplets of 2 μL on the fibre surfaces. At least five independent determinations at different sites of one sample were averaged and standard deviations were obtained.

Pure water flux experiments were conducted in a U-like membrane module filtration apparatus. For each module, ten fibres with 20 cm length were assembled into the filtration module and pure water flux measurement was performed in a cross flow mode through inside-out configuration. Each membrane sample was tested at least three times; the average value and the standard deviations were obtained. The hollow fibres were then tested for filtration using a dextran mixture of different molecular weights (10,000–150,000 Da). After completing the pure water flux experiments (as mentioned above), the dextran solutions were circulated through the membrane modules for 30 min. In this study, the feed temperature was maintained constant at 20 ± 2 °C, the solute concentration at 1.0 g/L and the feed pressure at 1 bar when testing all the membranes.

![Fig. 3. Viscosity of the polymer solution.](image)

![Fig. 4. Overall and partial cross-section SEM images of PVDF hollow fibre membranes prepared from (a) 1 wt%, (b) 2 wt% and (c) 3 wt% copolymer at 30 cm air gap.](image)
Gel permeation chromatography (GPC-50 system, Polymer Laboratories Ltd) was used to analyse the molecular weight cut off (MWCO) of the hollow fibre membranes. The system was equipped with a triple detector assembly: refractive index, viscosity and light scattering (15° and 90°). A guard column (PL aquagel-OH Guard 8 μm) and two columns (PL aquagel-OH MIXED-H 8 μm) for analysing broad range of molecular weights were used in series to separate the polymer molecules based on their hydrodynamic volume. The mobile phase was 0.1 M NaNO₃ and 0.01% w/w NaN₃ in DI water, the flow rate of 0.7 mL/min remained constant for all measurements. The eluent was filtered three times through 0.1 um anodisc Millipore filters (Millipore Co.) prior use in order to remove any contamination that would otherwise interfere with the light scattering detector. All measurements were performed at 25 °C in an air-conditioned room. The chromatographs were analysed using commercial GPC software PL Cirrus Multi (Polymer Laboratories Ltd.). The molecular weight distribution against the concentration curve of the feed dextran mixture (with the concentration of 1.0 g/L) and permeate were obtained from the GPC. The molecular weight of the dextran at which the concentration ratio of the permeate to the feed was equal to 10%, was reported as the molecular weight cut off.

Bovine serum albumin (BSA) was used as a model protein to evaluate the fouling resistance properties of the prepared membrane. Membrane was first pre-compacted at a trans-membrane pressure (TMP) of 1.5 bar for 30 min and the pure water flux was measured for every 5 min at a TMP of 1.0 bar. Then the deionised water was replaced with 1.0 g/L BSA in PBS solution for the fouling resistance test until 10 mL of permeate were collected.

Fig. 5. Overall and partial cross-section SEM images of PVDF hollow fibre membranes prepared from (a) 1 wt%, (b) 2 wt% and (c) 3 wt% copolymer at 0 cm air gap.

Fig. 6. Static contact angle measurement.
The values of permeate flux at the start and at the end of the protein filtration were recorded. After the protein filtration, the hollow fibre was cleaned with deionised water, and the water flux was measured again. This experiment was performed on the hollow fibres spun at 30 cm air gap and the rejection rate ($R$) of each membrane was calculated by the following equation:

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

where $C_p$ and $C_b$ were protein concentrations in permeate and feed (mg/mL), respectively. The values of $C_p$ and $C_b$ were determined using a UV–vis spectrophotometer (UV-2101PC, Shimadzu, UK) at a fixed wavelength of 280 nm.

Tensile strength and elongation at break of the hollow fibres were measured by Instron 4466 tensile test machine with a load cell of 1 kN, at a constant elongation velocity of 10 mm/min at room temperature of 20 ± 2°C. At least 5 fibres with 15 mm length were tested and the average data were taken for each sample. The deviation between the sample values and the average value was less than 5%.

3. Results and discussion

3.1. FTIR-ATR analysis

PVDF hollow fibre membranes were successfully spun from a polymer solution containing the amphiphilic graft copolymer, PVDF-g-PEGMA. Note that
during preparation of spinning solution from amphiphilic graft copolymer, the conventional steps of purifying the copolymer, i.e., precipitation, filtration and drying process were abolished [23]. Since our aim is to produce surface modified hollow fibres via an in-situ grafting with improved hydrophilic properties, we do not intend to characterise the synthesised graft copolymer PVDF-g-PEGMA as the copolymer's characteristics and properties have been previously studied in detail [13,25]. However, FTIR analysis was performed as to verify the existence of PVDF-g-PEGMA in the produced fibres. The FTIR spectra of the hollow fibres and PEGMA are presented in Fig. 1.

Comparing the IR spectra of fibres containing PVDF-g-PEGMA (Fig. 1-I-(b-g)), with IR spectrum of pure PVDF hollow fibre membrane (Fig. 1-I-(a)), two significant peaks appear and differ from the latter membrane. The IR spectra for all the fabricated fibres contain the characteristics band of C=O stretch and C–O–C stretch, which were represented by peaks at 1727 cm⁻¹ and 1100 cm⁻¹, respectively. These two peaks could not be observed in the IR spectrum of pure PVDF fibre. These peaks are similar to the ones obtained from the previous study on grafting of poly(ethylene glycol) methyl ether methacrylate onto PVDF membranes [25], hence suggesting the presence of the PVDF-g-PEGMA in and on the surface of the hollow fibres. In addition, no obvious peak could be observed at 1642 cm⁻¹ attributed to the C=C stretch (Fig. 1-II), which indicates that the unreacted monomer resulted from the polymerisation might have been completely removed through ethanol treatment. It is worth noting that ethanol was employed to prevent membrane shrinkage, and to remove the unreacted monomer since ethanol has been claimed to be a good solvent for PEGMA [25].

3.2. Effect of air gap distance on the membrane morphology

It is well known that the air gap distance is one of the most important spinning parameters that influence the ultimate hollow fibre membrane morphology and structure. Nevertheless, the mechanism behind spinning of hydrophilically modified PVDF membrane solution is still poorly understood. For the purpose of investigating the effects of air gap distance on the hydrophilic PVDF hollow fibre membranes, PVDF hollow fibre membranes with the addition of the amphiphilic graft copolymer mixture (estimated graft copolymer 1.5 wt%) were spun. The air gap was changed from zero, 10 cm and 30 cm, while the extrusion speed was kept at a constant rate (Table 1). The overall and partial cross section morphology SEM images for the spun hollow fibres were shown in Fig. 2.

The hollow fibre spun with 30 cm air gap exhibits long and large finger-like voids initiated from inner skin layer across the fibre, where this finger-like voids contribute approximately 90% of the overall fibre thickness. The remaining 10% is occupied by a very short finger-like structure near the inner layer and almost none near the outer layer. The outer surface is exposed for a longer period of time due to the presence of a high air gap. Thus, the polymer precipitation process occurs near the inner surface rather than the outer surface. As the dope solution consists of PVDF-g-PEGMA, the hydrophilic side chains of PEGMA might have quickly moved towards water near the inner surface causing a rapid liquid–liquid demixing process. In addition, the excess of hydrophilic PEGMA monomer in the dope solution might rapidly leach out into the internal water coagulant from the inner surface of the fibre (as this part is first brought into contact with water through lumen), resulting in the formation of macrovoids observed in the hollow fibre membrane.

When the air gap is reduced to 10 cm, the membrane structure changes significantly compared to the one spun at higher air gap, where it forms dual structure consisting of sponge-like central layer sandwiched by two finger-like structures of both sides or commonly referred to as “sandwich-like” structure. At a lower air gap distance, the fibre is rapidly immersed in the coagulation bath, after exiting from the spinneret. Therefore with relatively less evaporation time, the rapid exchange between non-solvent and solvent has occurred at both surface sides of the fibre, resulting in the formation of high volume of finger-like voids.

Fig. 9. FESEM images (a), (b) and (c) outer surface of samples F1-0, F2-0 and F3-0, respectively and (d), (e) and (f) inner surfaces of samples F1-0, F2-0 and F3-0, respectively.
near the outer skin layer. It can be observed that the length of the finger-like structure near the outer skin layer increases at a lower air gap, while the ones near the inner skin layer is decreased. Both finger-like voids do not exhibit similar size and length, whereas the fingers near the inner skin layer is observed to be relatively longer and larger from the outer skin layer. This is because the outer layer is exposed to air for a period of time before immersion in the external coagulation bath. Thus, the rate of precipitation near the outer layer is comparatively slower than the inner layer.

Nevertheless, the size and length of the finger-like structure becomes more or less equal when wet spinning (zero air gap) is introduced during spinning. Both outer and inner surface sides have finger-like structures of similar length and size, and between these finger layers there exists a central layer of sponge-like structure. Because the fibre is spontaneously immersed into internal and external coagulation baths consisting of pure water, the rate of precipitation for both surfaces is anticipated to be almost equal and fast, resulting in the similar structures of both side surfaces.

3.3. Effect of graft copolymer addition on solution viscosity

Apart from spinning parameters or factors such as the coagulation medium used or spinneret size etc., viscosity is one of the important factors in determining the spin-ability of the dope solution during the spinning of the hollow fibre membranes. Furthermore, the kinetics aspects of the membrane formation process are also controlled by the solution’s viscosity, since the solution’s viscosity has a strong influence on the inter-diffusion solvent and non-solvent during phase inversion process.

Fig. 3 shows the viscosity of the dope solution with the addition of the amphiphilic copolymer, PVDF-g-PEGMA. Viscosity of the PVDF solution increases from 2450 cP to 6440 cP with the addition of 1 wt% copolymer. However, when the composition of copolymer is raised to 2 wt% and 3 wt%, the viscosity increases dramatically to 21000 cP and 41600 cP, respectively, which demonstrates that starting from this point, a slight increase in the copolymer concentration may cause a drastic increase in the solution’s viscosity. The relationship between the solution’s viscosity and copolymer concentration does not rise proportionally due to the increase of unreacted monomer in line with the copolymer concentration in the solution.

Ideally, the viscosity obtained in this study can be considered as within the acceptable range for hollow fibre spinning, though further increase in the copolymer concentration might increase the solution’s viscosity, which may aid the spinning process of the hollow fibre membrane. However, in our study, a further increase of the copolymer concentration to 5 wt% in the spinning solution causes the solution to become gel. It is believed that when 5 wt% of copolymer is added into solution, the total amount of unreacted monomer, catalyst and ligand eventually becomes 45 wt% (largely associated with unreacted monomer because the catalyst and ligand amount accounts for 0.04 wt% and 0.2 wt%, respectively) of the total solution, where in this experiment 10 g of copolymer mixture yield 1 g of copolymer.
As a result, the solvent power (in this case NMP) is reduced due to the presence of excess monomer which causes the solution to be gelled. In addition, the presence of hydrophilic PEGMA monomer could also lead to the hydrophilic–hydrophobic interaction between the PEGMA and PVDF polymer in the solution which may induce inhomogeneity of the solution. Therefore, the copolymer concentration of up to 3 wt% in solution would be an acceptable range for preparing the dope solution from the amphiphilic graft copolymer.

3.4. Effect of graft copolymer concentration

3.4.1. Membrane morphology

Figs. 4 and 5 show the overall and partial cross section SEM images of hollow fibre membranes prepared from 1 wt%, 2 wt% and 3 wt% spun at 30 cm air gap and zero air gap, respectively. As seen from Fig. 4, hollow fibres containing 1 wt% and 2 wt% amphiphilic copolymer, PVDF-g-PEGMA exhibit an almost similar morphology where short finger-like structure exists near both the inner and outer skin of the fibre with long and large finger-like structures (macrovoids) present in between them.

On the other hand, the morphology of the hollow fibre membrane changes significantly when the copolymer concentration is raised to 3 wt%. The size of macrovoids that exist in 3 wt% fibre is remarkably reduced; however, the length of short finger-like structure near the inner skin increases two-fold in comparison with the fibres containing lower composition of PVDF-g-PEGMA. It is also observed that there exists a dense layer near the inner and outer skin of the former membrane. It is believed that the presence of hydrophilic graft copolymer, PVDF-g-PEGMA the excess monomer, PEGMA and PVDF contained in the spinning solution may have induced the occurrence of hydrophobic and hydrophilic repulsions, and hence resulting in this kind of membrane morphology [23]. Comparing with our previous work on flat sheet membrane, the turning point of the hydrophobic and hydrophilic repulsions occurred at the membrane containing 2 wt% graft copolymer, while for hollow fibre membrane developed in this study shows the changes at 3 wt% graft copolymer.

Nevertheless, it is worth mentioning that the conditions to fabricate flat sheet membranes and hollow fibre membranes can be considered as totally different from each other, therefore it could not be the basis of comparison. Hollow fibre membranes spun using the wet spinning method also show similar trends of morphology, as seen in Fig. 5. Although all membranes spun at zero air gap exhibit dual structures, which consist of a finger-like structure near the inner and outer layer with sponge-like structure in between them, the size of the largest finger-like structure is observed in the membrane containing 2 wt% PVDF-g-PEGMA.

3.4.2. Contact angle measurements

Contact angle is one of the widely used characterisation methods for determining the hydrophilic properties of a membrane. In this study, static contact angle measurements have been performed on the outer layer of the hollow fibre membranes, and the results are shown in Fig. 6. White bars represent the contact angle for hollow fibres spun at a 30 cm air gap, while the grey bars represent the contact angle for the hollow fibre membranes spun at zero air gap. Overall, the contact angle for all fibres falls in the range between 52.1° and 67.5°. Thus the results demonstrate that the prepared hollow fibre membranes show improvement in the hydrophilicity, as the pure PVDF membrane generally has a contact angle of 90° or above. Membrane contact angle decreases when the

<table>
<thead>
<tr>
<th>Hollow fibre</th>
<th>Composition</th>
<th>Spinning parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PVDF (%)</td>
<td>Copolymer (%)</td>
</tr>
<tr>
<td></td>
<td>Ethanol (%)</td>
<td>NMP + unreacted POEM + CuCl + DMDP (%)</td>
</tr>
<tr>
<td>FE-1</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>FE-2</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>FF1.5</td>
<td>22</td>
<td>2</td>
</tr>
<tr>
<td>FF10</td>
<td>22</td>
<td>2</td>
</tr>
<tr>
<td>FF20</td>
<td>22</td>
<td>2</td>
</tr>
</tbody>
</table>

Fig. 12. Cross section and inner surfaces of PVDF hollow fibre membranes spun with (a) 20 wt% NMP and (b) 30 wt% NMP, in water mixture as internal coagulation medium.
amphiphilic copolymer concentration is gradually increased from 1 wt% to 3 wt%. This is as expected due to the greater amount of hydrophilic PVDF-g-PEGMA present in the resulting membranes. Nevertheless, hollow fibres spun at zero air gap show a lower contact angle compared to the fibres spun at 30 cm air gap distance, which demonstrates that the former possesses higher hydrophilicity than that of the latter. When the hollow fibre is spun at the zero air gap, both the inner and outer surfaces of the fibre were brought into contact with water simultaneously, creating an opportunity for the hydrophilic side chains of the amphiphilic copolymer to self-segregate onto both surface sides. On the other hand, the latter membrane was exposed to air at a certain period of time (air gap distance of 30 cm) before immersion into a coagulation bath; hence this might have suppressed the degree of surface segregation of the amphiphilic copolymer on the outer surface.

3.4.3. Pure water flux measurements, dextran and BSA rejections

Pure water flux measurements, dextran and bovine serum albumin (BSA) data are presented in Fig. 7, Fig. 10(a) and Fig. 10(b), respectively. From Fig. 7, all hollow fibres show higher pure water flux than that of pure PVDF membrane. At least 60-fold increment of pure water flux was obtained from the modified hollow fibres show higher pure water flux than that of pure PVDF membrane. At 408, all hollow fibres show higher pure water flux than that of pure PVDF membrane. At least 60-fold increment of pure water flux was obtained from the modified membrane than that of pure PVDF. The highest water flux (123.4 L/m² h) is shown by the 2 wt% PVDF-g-PEGMA fibre spun at zero air gap.

Overall, the hollow fibres prepared without an air gap show greater water flux than the ones spun at 30 cm air gap. This is due to the fact that the fibres prepared at zero air gap would undergo rapid precipitation when brought into contact with water as internal and external coagulants, hence promoting the amphiphilic graft copolymer PVDF-g-PEGMA to be quickly self-segregated onto the inner and outer surfaces of the membranes. With the presence of the amphiphilic copolymer at both surface sides, more water would be attracted to pass through the membranes resulting in the higher water flux. On the other hand, membranes prepared from a 30 cm air gap have been exposed to air for a period of time (corresponding to the evaporation time for flat sheet membranes), thereby resulting in relatively less amount of PVDF-g-PEGMA self-segregating onto the membrane especially on the outer surface. As a result, the water flux is reduced for the latter membranes. This is also supported by the FESEM images presented in Figs. 8 and 9, where the hollow fibre membranes spun at zero air gap show a greater surface roughness on both inner and outer surfaces compared to the ones spun at 30 cm air gap.

By increasing the copolymer contents from 1 wt% to 2 wt%, the water flux increases for both membranes irrespective of their air gaps. This is attributable to the higher composition of the amphiphilic copolymer contained in that particular hollow fibre; hence attracting more water to penetrate through it. However, when the copolymer concentration is increased to 3 wt%, the water flux decreases significantly and is reduced to an even a lower value than the 1 wt% membrane. As explained in our previous work on flat sheet membranes [23], 3 wt% membrane has a lower water flux among all attributed to the compact and compressed type of membrane morphology (based on SEM images), hence the water penetration across the membrane is hindered.

Dextran MWCO experiments have been performed using 1.0 g/L of dextran solutions from the mixture of different molecular weights (10,000–150,000 Da) on the hollow fibre membranes spun at 30 cm air gap, and the results are demonstrated in Fig. 10(a). As seen in Fig. 7 and Fig. 10(a), the trend of dextran rejections is consistent with the pure water flux measurement, for which membranes with lower water flux possess a greater dextran rejection. Hollow fibre membrane prepared from 3 wt% copolymer and spun at 30 cm air gap shows the highest rejection of dextran among all, and this result is in agreement with the pure water flux data and membrane morphology. BSA rejection also shows similar trend with the dextran rejection. The highest BSA rejection data was found from the hollow fibre prepared from 3 wt% PVDF-g-PEGMA with 93.2% rejection, while the lowest rejection was demonstrated by the hollow fibre prepared from 2 wt% PVDF-g-PEGMA with 77.8% rejection (Fig. 10(b)). All membranes demonstrated 100% flux recovery upon washing with deionised water after the BSA filtration experiment.

3.4.4. Mechanical properties

The mechanical properties of the prepared hollow fibre membranes have been evaluated through tensile strength and elongation measurements. Fig. 11(a) and (b) show the results of tensile stress at break and elongation at break of the hollow fibre membranes, respectively. Fig. 11(a), as expected, revealed that the tensile stress of hollow fibre membranes decreases with the increase of copolymer concentration from 1 wt% to 2 wt%, then again increases from 2 wt% to 3 wt%.

From membrane morphological aspect, 2 wt% fibre possesses the highest volume of macrovoids among all (as observed from SEM images in Figs. 4 and 5), therefore leading to the weakest mechanical strength among all, especially when spun at higher air gap of 30 cm. Overall, the tensile strength of membranes spun at zero air gap are higher than the ones spun at higher air gap and this phenomenon could be correlated with the membrane morphological point of view (as previously discussed in the Section 3.2). Although the former membranes

Table 3

<table>
<thead>
<tr>
<th>Hollow fibre</th>
<th>Pure water flux (L/m² h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FE-1</td>
<td>391.3</td>
</tr>
<tr>
<td>FE-2</td>
<td>406.2</td>
</tr>
<tr>
<td>FF1.5</td>
<td>171.1</td>
</tr>
<tr>
<td>FF10</td>
<td>112.5</td>
</tr>
<tr>
<td>FF20</td>
<td>50.7</td>
</tr>
</tbody>
</table>

Fig. 13. Overall and cross section SEM images of PVDF hollow fibre membranes prepared from (a) 1.5 mL/min and (b) 10 mL/min dope extrusion rate.
contain a dual structure consisting of finger-like structure occurring at both surface sides, the size of macrovoids is much smaller than that of the latter as observed from the SEM images, and this provides a greater tensile strength. The elongation at break as shown in Fig. 11(b), are observed to be substantially higher for the membranes spun at zero air gap. The maximum elongation that could be obtained is from the 2 wt% hollow fibre membrane, which is in accordance with the tensile strength result (lower tensile strength usually results in higher elongation at break, or vice versa).

From these results, all hollow fibre membranes exhibit ductile behaviour in terms of mechanical properties, as demonstrated by the relatively small tensile strength and large extension at break. The tensile strength of the modified membranes falls in the range between 2.2 MPa and 5.9 MPa, while the elongation at break demonstrated the values between 146% and 234%.

3.5. Effect of ethanol addition in spinning solution

The preparation of hydrophilic PVDF membrane containing the amphiphilic graft copolymer via the in-situ grafting of spinning solution has resulted in the improvement of pure water flux and anti-fouling properties. However, membrane morphology contains a large volume of macrovoids. Macrovoids can cause defects in membranes, consequently decrease the membrane rejection as well as the mechanical strength.

As an effort to suppress the macrovoids formation in membranes, 5 wt% ethanol has been added into the dope solution. Ethanol is a weak co-solvent that often being employed as a non-solvent additive in the preparation of PVDF membrane solution [26,27]. Furthermore, since ethanol was found to be the good solvent for dissolving PEGMA [25], the presence of ethanol in the spinning solution is anticipated to be effective in removing the unreacted PEGMA from the resulting PVDF membrane. The detailed preparation and spinning conditions of the PVDF hollow fibre membranes prepared with ethanol and copolymer additions are tabulated in Table 2. Two similar fibres were spun, where the preparation and spinning conditions were identical except that different fractions of NMP in water mixture were employed as the internal coagulation medium.

Fig. 12 shows the cross section and inner surface morphology of hollow fibre membranes spun with the addition of ethanol. Porous inner structure could be observed from the SEM images of both hollow fibre membranes spun with the addition of ethanol and the presence of NMP/water mixture as the coagulation medium. The size of finger-like structure presence in the inner surface of both hollow fibres becomes relatively smaller when compared to the ones previously prepared with different conditions (Fig. 4(b)). It is believed that the growth of macrovoids had been suppressed and more porous inner surface has been formed by adding ethanol into the spinning solution and due to the employment of NMP/water mixture as internal coagulation bath.

From Table 3, it can be seen that membrane performance in terms of pure water flux has been remarkably improved to approximately 400 L/m² h at 1 bar (FE-1 and FE-2) with the ethanol addition and NMP/water mixture as an internal coagulation bath medium. Ethanol can act as a pore former, as reported by Kesting [28]. The addition of ethanol is believed to have leached out and at the same time enhances the leaching out process of the unreacted PEGMA from the resulting membranes during phase inversion process. Similar to the observation by Yeow et al. [29], the addition of 5 wt% of ethanol into the dope solution had decreased the solution viscosity to 14,000 cP instead of 21,800 cP (without ethanol addition).

By employing a certain amount of NMP in the coagulation medium, a delayed liquid–liquid demixing has been imposed during membrane formation, thus resulting in the reduced length of the finger-like structure and porous skin layer. Combinations of these two factors have eventually resulted in more porous structure of the membrane, consequently improving the pure water flux.

3.6. Effect of dope extrusion rate

The effect of dope extrusion rate (or shear rate within a spinneret) during the hollow fibre spinning on membrane morphology, performance and mechanical strength has been investigated in this study, where the detailed preparation of the dope solution and spinning conditions are tabulated in Table 2. Dope extrusion rate has been varied from 1.5 mL/min, 10 mL/min and finally to 20 mL/min. Fig. 13 shows the cross section SEM images of hollow fibre membranes spun with the dope flow rate of (a) 1.5 mL/min and (b) 10 mL/min. It should be mentioned that the cross section morphology of hollow fibre membrane spun at 20 mL/min extrusion rate (FF20) did not differ significantly from the one spun at 10 mL/min (FF10). Therefore it is not shown here. It can be seen that the membrane spun at lower extrusion rate of 1.5 mL/min (FF1.5) exhibits large macrovoids initiated from the inner surface, for which the volume of the macrovoids is estimated to be almost 90% of the hollow fibre cross section thickness.

The remaining percentage consists of small and short finger-like structure near the outer surface of the fibre. On the other hand, the size of macrovoids decreases substantially when the extrusion rate is increased to 10 mL/min (FF10), where the overall wall thickness comprised of approximately 55% of macrovoids with smaller size near the inner surface, and relatively shorter and smaller finger-like structure presence near the outer surface. There exists sponge-like structure region in between these surfaces. By increasing the dope extrusion rate, greater molecular orientation is induced and the molecular chains are packed closely to each other, leading to a tighter structure during hollow fibre membrane formation [30].

Fig. 14 shows that the outer surfaces of all hollow fibres are dense irrespective of the extrusion rate employed. Water is a strong non-solvent which being employed as both internal and external coagulant, resulting in the instantaneous
liquid–liquid demixing leading to a denser skin during hollow fibre membrane formation. Nevertheless, membrane outer surface becomes rougher and some globule-like particles could be observed with the increase in the dope extrusion rate. The presence of hydrophilic PVDF-g-PEGMA and the excess monomer had further enhanced the rate of precipitation, hence promoting a higher degree of liquid–liquid demixing. Hence, greater surface roughness is observed on the hollow fibre membranes spun at higher dope extrusion speed. It is also observed that the hollow fibre outer diameter increases from 0.1 cm to 0.13 cm when the dope extrusion speed is increased from 1.5 mL/min (FF1.5) to 10.0 mL/min (FF10). However, further increment in dope extrusion rate to 20.0 mL/min results in 0.14 cm outer diameter, which can be considered as a minor change.

Pure water flux measurements of the hollow fibre membranes prepared with different dope extrusion rates are tabulated in Table 3. It clearly shows that the pure water flux decreases when the dope extrusion rate is enhanced. The performance results are consistent with the membrane morphology as discussed above, where higher extrusion rate results in a tighter structure which has higher resistance to water. Fig. 15 demonstrates the tensile strength at break of the hollow fibre membranes with different extrusion rates. Detailed verification of this aspect is beyond the scope of the present study.

4. Conclusions

PVDF hollow fibre membranes containing an amphiphilic graft copolymer, PVDF-g-PEGMA have been successfully spun through the direct preparation from polymerisation, or address herein as the in-situ grafting of spinning solution. The hollow fibres have shown improvement in the hydrophilicity and fouling resistance properties. Pure water flux of the modified membranes has been significantly increased to approximately 400-fold higher than pure PVDF membrane, while the contact angle has been reduced to around 60°. The highest pure water flux 406.2 L/m² h was obtained from the membrane prepared with ethanol addition and 30 wt% NMP in water as internal coagulant. In general, hollow fibres spun at zero air gap showed greater water flux than the ones spun at higher air gap, this could be due to the relatively larger distribution of the surface segregated amphiphilic copolymer, PVDF-g-PEGMA on the inner and outer layer of the former hollow fibre membranes. It is also observed that the morphology of the hollow fibre membranes changed significantly at different air gap distance. The hollow fibre membranes spun through wet spinning method exhibit a relatively smaller volume of macrovoids compared to the ones spun at the higher air gap, thus providing better mechanical properties. With increasing dope flow rate, the hollow fibre membrane possesses less macrovoids and better tensile strength due to a greater molecular orientation and closer package of molecules. By varying the parameters involved during the preparation of spinning solutions and spinning process itself, various effects on the ultimate properties and performance of surface-modified PVDF hollow fibre membranes can be observed.

Acknowledgements

The authors gratefully acknowledge the research funding provided by EPSRC in the United Kingdom (grant No. EP/D068851/1), the Ministry of Higher Education Malaysia, University of Malaya (RG120/11AET), and Dr. Yutie Liu for their support and contribution to this project.

References


