Morphologies and separation characteristics of polyphenylsulfone-based solvent resistant nanofiltration membranes: Effect of polymer concentration in casting solution and membrane pretreatment condition

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Abstract−The performance of polyphenylsulfone (PPSU) solvent resistant nanofiltration (SRNF)-based flat sheet membranes prepared from phase inversion method was investigated by varying the concentration of polymer in the dope solution and condition of membrane pretreatment process. The membrane properties were characterized by SEM, FTIR, AFM and contact angle goniometer, while their performance was evaluated by measuring methanol flux and rejection of different molecular weight of dyes (ranging from 269 to 1,470 g/mol) in methanol. The experimental results showed that the polymer concentration has great impact not only on the final membrane morphology but also its separation characteristics. Increasing polymer concentration from 17 to 25 wt% tended to suppress finger-like structure and more pear-like pores were developed, causing methanol flux to decrease. This can be explained by the decrease in molecular weight cut off (MWCO) of the membrane prepared at high polymer concentration. With respect to the effect of membrane pretreatment conditions, the rejection of membrane was negatively affected with longer immersion period in methanol solution prior to filtration experiment. The variation in membrane rejection can be attributed to the rearrangement of the polymer chain, which results in membrane swelling and/or change of membrane surface hydrophilicity.

Keywords: Polyphenylsulfone, Solvent Resistant Nanofiltration, Methanol Flux, Dye Rejection, Membrane Pretreatment

INTRODUCTION

Separation processes are essential to many industrial fields such as chemical, oil refining, material processing, etc. Separation technologies are critical to achieve high purity of active compounds or end products, reduce waste and improve efficiency of raw materials [1]. Over the past three decades, membrane separation, which uses membrane as filter, has become a distinguished separation technology, providing effective alternative to competitive technologies such as distillation, adsorption, extraction and ion exchanger. Compared with the conventional technologies, membranes offer greater advantages, for instance, less energy consumed, no additives required and low operational cost [2,3].

Among various membrane processes, nanofiltration (NF) which its application can be divided into two types, aqueous and non-aqueous systems, holds enormous potential in various industrial applications. NF is a pressure-driven process that has been introduced initially to aqueous systems primarily for water purification and other water-related treatments [4-8]. For non-aqueous systems, NF membranes known as solvent resistant nanofiltration (SRNF) have captured more attention since they provide effective separation of compounds dissolved in solvents with greater range of molecular weight (200 to 1,400 g/mol) without hindering simultaneous passing of the solvent. Therefore, the SRNF-based technologies are

capable in recovery of solvent in lube oil dewaxing processes [9], degumming of vegetable oil [10], reuse of extraction solvent in the food industry [11] and purification of pharmaceutically active ingredients [12].

The phase inversion process, which was first introduced by Loeb and Sourirajan [13] in the 1960s, is the fundamental principle in the synthesis of the most integrally skinned asymmetric polymeric membranes including SRNF membranes. In this process, a thermodynamically stable polymer dope solution is transformed from a liquid into a solid state induced by immersion precipitation (immersion in non-solvent bath). The polymer dope solution consists of a polymer and a solvent, but may also consist of a third component (e.g. additives and co-solvent). The formation of asymmetric membranes depends on kinetic and thermodynamic parameters. The kinetic parameters refer to exchange rate between solvent and non-solvent, and kinetics of phase separation, whereas the thermodynamic parameters are related to polymer-solvent interactions, solvent/non-solvent interactions, and interfacial stability [14]. In addition, many experimental parameters, including composition of polymer dope solution, evaporation time, coagulation medium and post-treatment known to have an influence on the final structure of the membrane obtained at the end of the phase inversion process, thus have an impact on membrane morphologies and separation performance of the membrane. Therefore, the materials selection of polymers, solvents and non-solvents is very important to tailor membranes to fit the intended applications [14]. Those parameters influence the final morphology of the membrane, which eventually affects the performance. For example, higher polymer concentration pro-

duced membranes with thicker and denser skin-layer with lower porosity, thus leading to higher selectivities but lower permeabilities [15]. Furthermore, molecular weight cut off (MWCO) of a membrane could be altered by polymer concentration of the dope solution in which an increase in polymer concentration leads to a lower MWCO [16]. Besides, increasing evaporation time before immersion in the coagulation bath could generally produce denser skinlayers [39].

Up to now, most of the SRNF research works have focused on (a) unraveling solvent and solute transport mechanisms, (b) improving membrane stability in various types of solvent and/or (c) tailoring membrane pore size/MWCO. Only little attention is paid to membrane pretreatment, although several researchers have reported that it could enhance or decrease the membrane flux [17, 20]. For instance, van der Bruggen et al. [18] observed a significant change in water flux of the commercial hydrophobic membrane (MPF-50, Koch Membrane Systems) after the membrane was pretreated with pure ethanol for ten days prior to testing. The flux of the membrane was increased from 6.5 to 22.6 L/m^2·h after the pretreatment process, and this enhancement was attributed by the authors to rearrangement of polymer chains at the membrane top layer. It was further established that a hydrophilic groups in the membrane tended to form small 'clusters', making the membrane became locally hydrophilic [19]. Other than the change in solvent flux, Darvishmanesh et al. [20], on the other hand, have reported the variation of dye rejection of a commercial membrane (StarMem, Membrane Extraction Technology Ltd.) after the membrane was subjected to pretreatment process using polar solvents (e.g., acetone, acetic acid, and methanol) for a week. They attributed the change in membrane filtration performance (decrease in rejection but increase in solvent flux) to the changes in membrane intrinsic properties such as its surface hydrophobicity and reorganization of the membrane material itself.

Many relevant research works utilize the commercial SRNF membranes that are well-known for their compatibility with a wide range of solvents. These membranes include the Koch SelRO® membranes (Koch Membrane Systems), DuraMem® and PuraMem® series (Evonik's Membrane Extraction Technology Ltd.), SolSep membranes (SolSep BV) and Inopor series (Inopor® GmbH). Other than these commercial membranes, polymeric materials such as polyimide (PI) [21-23], polyamide (PA) [24], polyacrilonitrile (PAN) [25], polydimethylsiloxane (PMDS) [26,27] and polyelectrolyte

(PE) complexes [28] are also considered in SRNF membrane making. Although polyphenylsulfone (PPSU) (see Fig. 1) is relatively new in the polysulfone family, it shows huge potential as a membrane for different applications, such as fuel cell [29], pervaporation [30], gas separation [31] and water treatment process [32]. The PPSU which comprises sulfone moieties, ether linkages and biphenyl group in its repeat group have the highest impact strength compared with the other family members [33]. It presents superior resistant to hydrolysis and plasticization of stress cracking. Its thermal and mechanical stability, chemical resistance and ease of manufacturing also make PPSU a remarkable candidate as SRNF membranes [34].

A study of PPSU membranes in organic solvents was first reported by Darvishmanesh et al. [33] in 2011. They investigated the effects of different membrane preparation conditions (i.e., solvent types and polymer concentrations) on methanol permeability and Rose Bengal rejection (MW=1,017.64 g/mol). Although these two parameters have been shown to have great influence on the membrane morphology and performance, a detailed discussion on the relationship between the membrane formation via phase inversion process as well as pretreatment conditions with the membrane performance has yet to be explored. For this reason, extensive studies of the parameters (polymer concentrations and pretreatment conditions) involved in the PPSU membrane preparation were carried out in this work. At first, the PPSU membranes made of different polymer concentrations (17, 21 and 25 wt%) were characterized with respect to morphology, surface roughness, contact angle and filtration separation capability. Then, selected PPSU membrane was subjected to different pretreatment conditions and the results were discussed in detail with respect to physico-chemical properties and separation performance. Different MWs of dyes in the range of 269-1,470 g/mol were used to characterize the MWCO of PPSU membranes and to investigate the separation behavior at different pretreatment conditions.

METHODOLOGY

1. Materials

PPSU polymer pellets with MW=50,000 g/mol and specific gravity of 1.29 (Radel R-5000 NT) were purchased from Solvay Advanced Polymers, United States. N-methyl-2-pyrrolidinone (NMP) was obtained from Merck, Malaysia and used to dissolve the polymer. Methanol (analytical grade, >99%), which was used to evaluate membrane performance and used as a pretreatment solvent, was supplied by Merck, Malaysia. Methanol was chosen due to its good
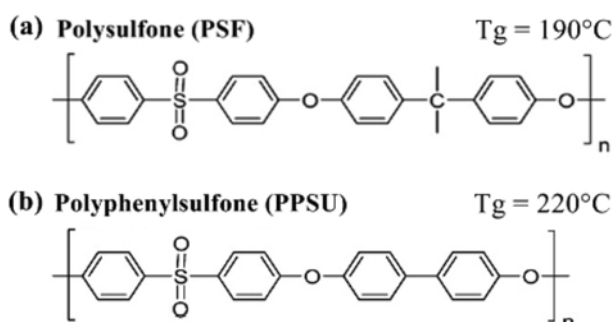

Fig. 1. Chemical structure of polysulfone (PSF) and polyphenylsulfone (PPSU).

(a) Polysulfone (PSF)　　　　　Tg = 190°C

(b) Polyphenylsulfone (PPSU)　　　Tg = 220°C

Table 1. Dye properties

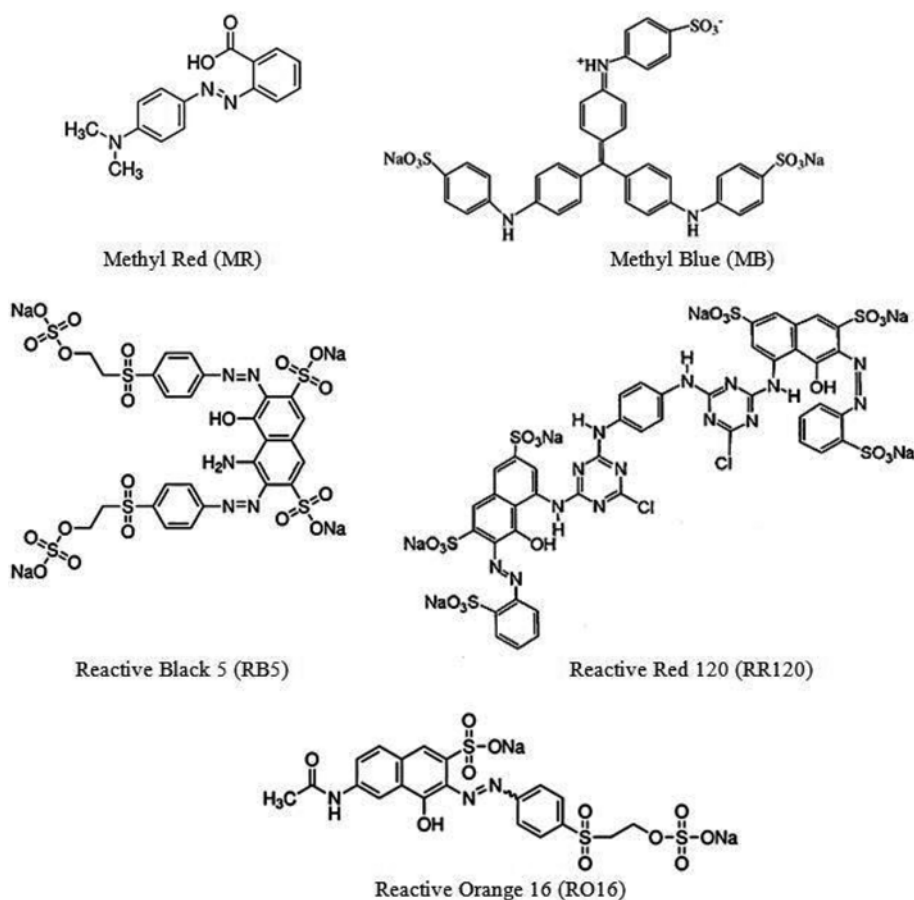| Dye	Molecular weight (g/mol)	Maximum absorption wavelength (nm)
Reactive red 120 (RR120)	1,470	539
Reactive black 5 (RB5)	991	592
Methyl blue (MB)	800	316
Reactive orange 16 (RO16)	616	494
Methyl red (MR)	269	496

Fig. 2. Molecular structure of dyes used in this study.

solubility in many organic solutes at high concentrations, easy availability and is common organic solvent in chemical and pharmaceutical industries [35]. Methyl red (MR), reactive orange 16 (RO16), methyl blue (MB), reactive black 5 (RB5) and reactive red 120 (RR120) purchased from Sigma-Aldrich, Malaysia were used for solute rejection experiments by dissolving them in methanol solution. The MW of dyes in methanol solution together with their maximum absorption wavelength are summarized in Table 1 and their organic structures are shown in Fig. 2.

2. Preparation of Membranes

Integrally skinned asymmetric PPSU membrane was prepared from polymeric casting solutions via a phase inversion method. Polymer pellets in pre-weighed quantity were first dissolved in NMP solvent at room temperature and stirred at least 20 h to ensure the polymer dissolution was complete and homogeneous. The solutions were then left for at least 24 h to remove air bubbles before membrane casting process. The polymer casting solution was cast on a glass plate without any non-woven support at room temperature. The membrane was subsequently immersed in a non-solvent water bath and kept for 24 h. Lastly, the membrane was air-dried for 24 h before it was subjected to testing.

Two synthesis parameters were investigated to determine their effects on the membrane morphology, properties and performance:

Series 1: *Influence of polymer concentration.* PPSU membranes of different properties were prepared from polymer dope solutions

Table 2. Condition for PPSU membranes pretreatment prior to testing

Designation	Solvent used in pretreatment	Membrane air-drying	Duration for solvent pretreatment
Control		Yes	1 min
Case 1		Yes	1 day
Case 2	Methanol	No	1 day
Case 3		No	7 days
Case 4		No	14 days

containing various PPSU concentrations: 17, 21 and 25 wt%.

Series 2: *Influence of membrane pretreatment condition using methanol.* PPSU membrane with 17 wt% polymer concentration was used for this investigation. The membrane was subjected to different pretreatment conditions as summarized in Table 2. Compared to control and case 1 membrane, other membranes (case 2-4) were post-treated with methanol without undergoing air-drying process.

3. Membrane Characterization

The membranes were characterized by scanning electron microscope (SEM) and contact angle goniometer. The morphology of the membrane was observed by SEM (TM3000, Hitachi, Japan). Samples of SEM analysis were prepared by fracturing the membrane in liquid nitrogen. Then, each sample was platinum-coated

in a specialized device to avoid surface charging during analysis. The hydrophilicity/hydrophobicity of the membranes was measured by contact angle goniometer (OCA15plus, DataPhysics, Germany), equipped with image-processing software. Ten different spots on the membrane sample were measured to yield an average value. The AFM measurement for membrane surface morphol-
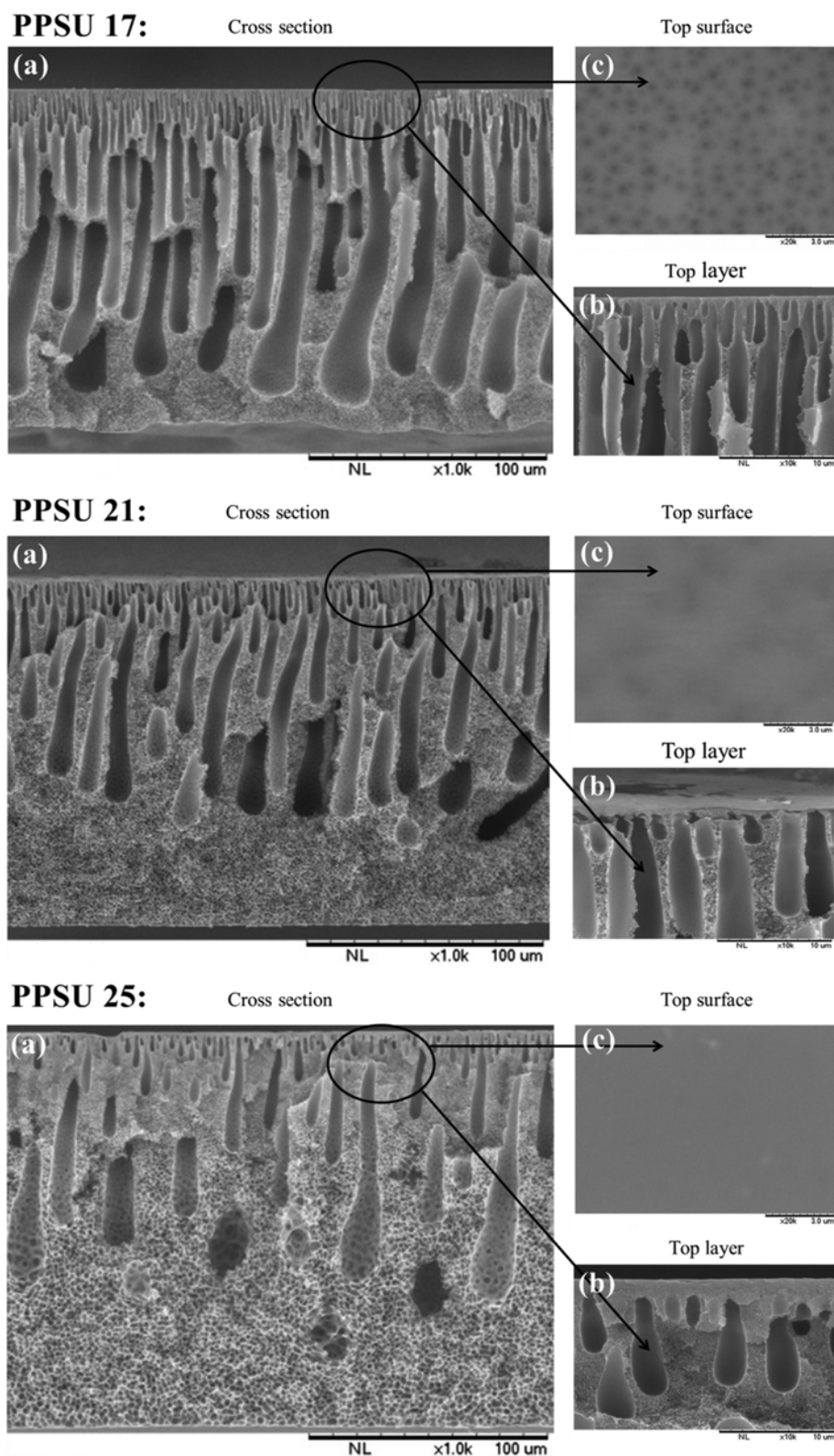

Fig. 3. SEM of PPSU membranes cast from 17, 21 and 25 wt% PPSU solution: (a) cross section; (b) top layer; (c) top surface.

ogy was carried out using a Multimode Nanoscope (Digital Instruments Inc., Santa Barbara, CA, USA). The roughness of membrane surfaces was obtained from the AFM images using NavoNavi Station software (version 5.01C). The surface roughness was expressed by a root-mean-square roughness (R_q) - average of height deviations taken from the mean data plane: $R_q = \sqrt{(Z_i^2/N)}$ where Z is the peak-to-valley difference in height values within the analyzed region. The scanning area of each membrane was 10 μm×10 μm. Fourier transform infrared (FTIR) spectra of the membranes were recorded with FTIR spectroscope (Nicolet 5700, Thermo Electron Scientific Instruments Corporation, USA) over a range of 4,000-700 cm^{-1}.

4. Filtration Experiments

The separation performance of the membranes with respect to permeability and solute rejection was evaluated using a stainless steel dead-end stirred cell (Sterlitech HP4750, Sterlitech Corporation, USA) with maximum capacity of 300 mL. A nitrogen cylinder equipped with a two-stage pressure regulator was connected to the top of the stirred cell to supply the desired operating pressure for filtration experiments. The operating pressure was controlled at between 5 and 25 bar for pure methanol flux measurement and 6 bar for all rejection experiments. All experiments were at room temperature. To minimize concentration polarization during the experiment, a Teflon-coated magnetic stirring bar was used and was controlled at 1,200 rpm on top of the active side of membrane. Membrane circular coupons were of 14.6 cm^2 (effective diameter: 4.3 cm). Prior to the experiments, the membranes were compacted at pressure of at least 26 bar for about 1 h. The membrane flux was collected after 30 min of experiment when flux had achieved steady-state and was measured every 10 min for up to 2 h. The flux, J (L/m^2·h) of membrane was determined by measuring volume of permeate (V) per unit area (A) per unit time (t) according to the following equation:

$$J = \frac{\Delta V}{A \Delta t} \tag{1}$$

With respect to dye rejection determination, the experiment was conducted by filtering methanol solution containing single dye compound (see Table 1) at initial solute concentration of 10 mg/L. The rejection rate, R (%), of the dyes by the membranes was calculated using the following equation:

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

where C_p is the dye concentration of permeates and C_f is the initial concentration. Concentrations of permeate and feed solutions were measured using UV-vis spectrophotometer (DR5000, Hach Company, USA). Blank wavelength scan with pure methanol was first performed prior to permeate sample analysis.

RESULTS AND DISCUSSION

1. Polymer Concentration

1-1. Properties of Membranes

The effect of polymer concentration on membrane properties with respect to morphology and performance was investigated. Fig. 3 presents the SEM images of the cross sectional structure and

top surface of the PPSU membrane prepared at a different polymer concentration. The membrane prepared from the dope solution of 17 wt% shows clear finger-like pores (Fig. 3 PPSU 17(a)), and with an increase of polymer concentration from 17 to 25 wt%, the pores are gradually suppressed into pear-like pores (Fig. 3 PPSU 25(a)). Also, the thickness of the membrane top layer for 17 wt% polymer concentration (Fig. 3 PPSU 17(b)) was slightly increased when the polymer concentration was increased to 25 wt% (Fig. 3 PPSU 25(b)). The increment in the polymer concentration caused a decrease in diffusion rate between the solvent and non-solvent
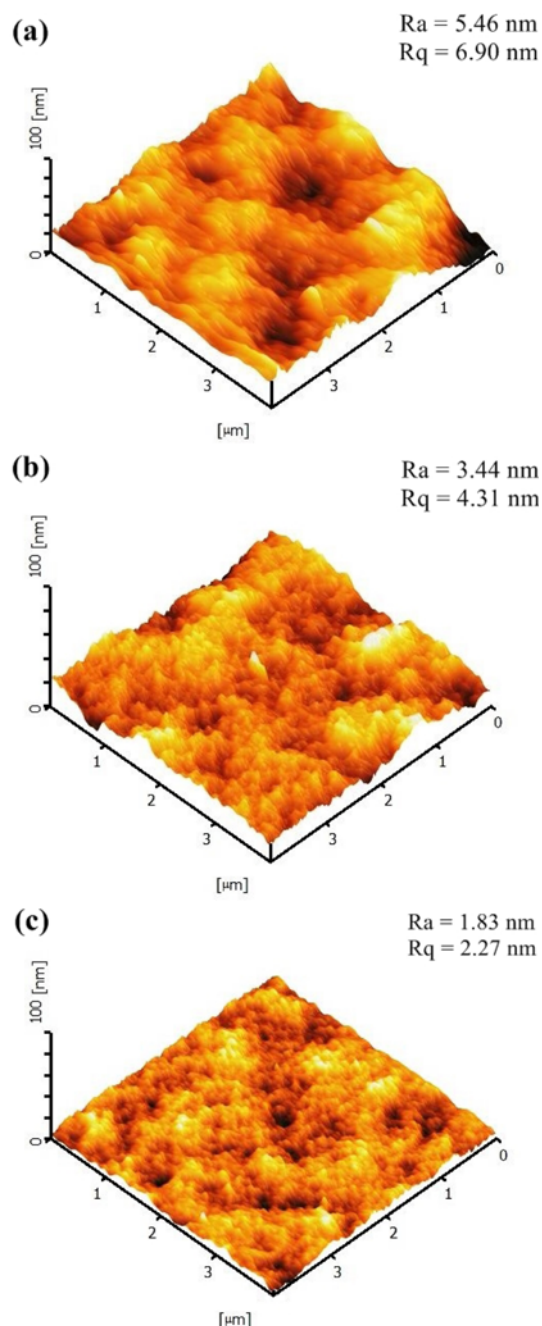

Fig. 4. AFM images of surface structure of PPSU membranes prepared with different polymer concentration (a) 17 wt%, (b) 21 wt% and (c) 25 wt%.

during the polymer precipitation process, forming a dense and relatively thick top layer [36-38]. From the top view of the membrane, the presence of micro valleys is clearly observed as their emergence as dark spots (Fig. 3 PPSU 17(c)) on the 17 wt% PPSU membrane. As can be seen from Fig. 3 PPSU 25(c), the distance between valleys enlarges and becomes invisible when membrane is made of highest PPSU concentration.

Fig. 4 indicates the AFM images of surface of PPSU membranes together with roughness values at a scan size of $4\,\mu m \times 4\,\mu m$. The brightest region represents the highest peak of the membrane surface, whereas the darkest regions indicate valleys. The result shows that the surface morphology of the membranes changes with concentration of polymer in the dope solution. The mean roughness (R_a) of the membrane is reduced from 5.46 to 1.83 nm with an increase in polymer concentration from 17 to 25 wt%. The reduction in surface roughness may be attributed in part to the reduction of the membrane pore size and porosity. To confirm this, the relationship between morphological structure and the membrane performance will be further considered in the next section.

Fig. 5 shows the influence of polymer concentration on the viscosity of the polymer dope solution prepared. As expected, increasing polymer concentration causes the viscosity of dope solution to increase. However, an exponential change in dope viscosity is observed when polymer concentration is increased from 21 to 25 wt%. The change in dope viscosity is an important parameter that could influence the kinetic aspect of phase inversion and the morphology of final membranes [14]. The kinetic aspect of phase inversion by immersion precipitation is related to exchange rate of solvent out of and water into the dope solution (mass transfer during coagulation) [37,39]. The increase in viscosity of the dope solution hinders the overall diffusion. As a result, it delays the exchange rate between solvent and water, which leads to a higher polymer concentration at the polymer-water interface during the precipitation process and suppresses macrovoid formation, as evidenced by SEM results (Fig. 3). Similar observation was also reported elsewhere [34,39,40].

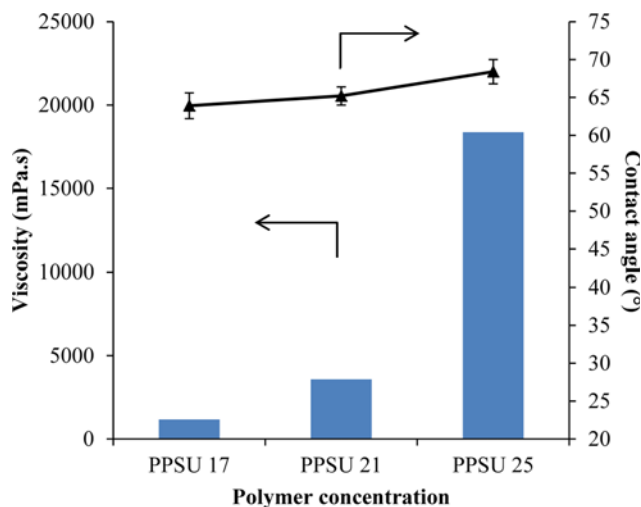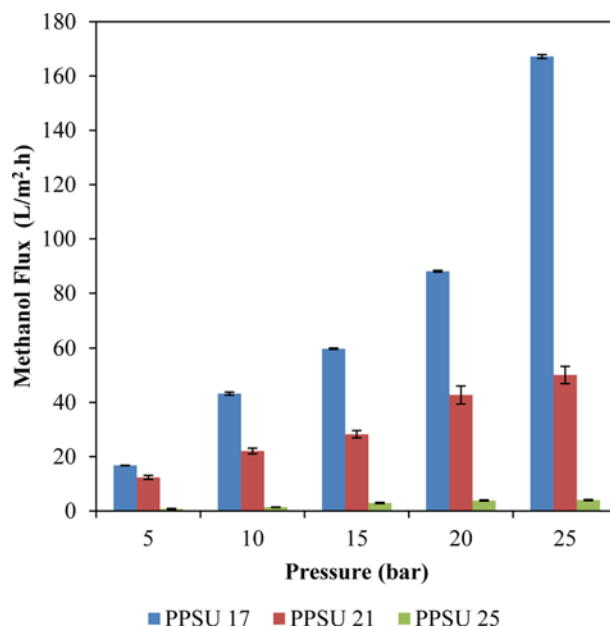Fig. 5 also shows the effect of polymer concentration on the con-

Fig. 6. Methanol flux of PPSU membrane as a function of operating pressure.

tact angle values of the PPSU membranes. The contact angle of PPSU membrane is only slightly increased from 63.9° to 68.4° with increasing polymer concentration from 17 to 25 wt%. The results suggest that the polymer concentration has insignificant role in affecting membrane hydrophilicity. The contact angle of the PPSU membranes, which falls between 64° and 68°, also revealed that PPSU membrane is semihydrophilic.

1-2. Performance of Membranes

The influence of the polymer concentration on pure methanol flux was studied in the operating pressure ranging from 5 to 25 bar. Based on Fig. 6, polymer concentration as well as operating pressure had a considerable influence on the methanol flux. For 17 wt% PPSU membrane, the flux increased from 16.8 to 167.2 L/m^2·h when pressure was increased from 5 to 25 bar. The flux improvement is expected as higher driving force is created for methanol to permeate faster at higher operating pressure. Similarly, the flux of membranes made of 21 and 25 wt% PPSU is increased with increasing operating pressure, although the extent of flux change in 25 wt% PPSU membrane is smaller than that of membranes made of lower polymer concentration.

Of the membranes tested, the flux tends to decrease as the polymer concentration increases. This can be explained by the fact of the increase in membrane intrinsic resistance resulted from reduced surface pore size and/or suppression of finger-like pores. At low polymer concentration, the pore size increases with increasing surface roughness; thus the membrane surface exhibits distinct peaks and valleys as confirmed by the AFM results (Fig. 4). The valleys provide paths of least resistance for the flux, which explains the relatively higher flux of the 17 wt% PPSU membranes [36]. Compared to the 17 and 21 wt% PPSU membrane, which is dominated by finger-like microvoids, the development of sponge-like morphology as shown in the 25 wt% PPSU membrane has played a role in increasing solvent transport resistance and reducing metha-
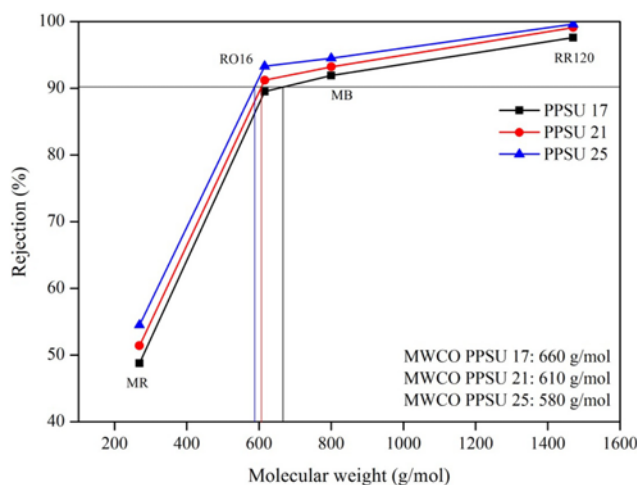

Fig. 5. Properties of fabricated PPSU membrane.

Fig. 7. Effect of polymer concentration on the MWCO in methanol at 6 bar.

Fig. 8. Effect of pretreatment process on pure methanol flux and rejection of RB5 (991 g/mol) and RO16 (616 g/mol) in methanol using PPSU membrane.

nol productivity. These results are consistent with the findings reported elsewhere in which increasing polymer concentration in the dope solution could result in lower organic solvent flux of membrane [16,34,40]. In addition, the results also show that the prepared membranes are able to sustain high operating pressure without collapsing, regardless of PPSU concentration, owing to the high mechanical stability of membranes prepared.

The molecular weight cut off (MWCO) is determined by plotting rejection of solutes against solute MW and interpolated to determine the MW at 90% rejection [40]. The MWCO trend for the PPSU membranes made of different polymer concentration is presented in Fig. 7. The MWCO of the membranes is determined using four different dyes with MW ranging from 269 to 1,470 g/mol. From Fig. 7, the dye rejection is increased with increasing dye MW, irrespective of polymer concentration. In addition, an increase in polymer concentration is observed to give a lower MWCO. The membrane MWCO is reported to decrease from approximately 660 to 580 g/mol by increasing polymer concentration from 17 to 25 wt%. The rejection trend for different polymer concentration is inversely proportional to methanol flux (Fig. 6) in which the higher the dye rejection the lower the methanol flux and vice versa. It seems that the finger-like dominated PPSU structure is highly favorable for increased flux of methanol, whereas the sponge-like is greater at rejection of dyes by increasing the resistance against methanol transport across the membrane. The increment in rejection with a decrease in flux was also observed by See-Toh et al. [16] for polyimide SRNF membrane.

2. Pretreatment Process

Membrane pre-treatment plays an important role in membrane performance for non-aqueous systems. Pretreating the membrane before testing becomes critical because the solvent-membrane interactions significantly affect the performance of the membrane. The purpose of pretreating the membrane with organic solvent is to make the membrane in stable condition prior to any experiment. It is because the sudden exposure of membrane to the solvent of filtration may result in inconsistent flux and sudden swell of membrane. We selected PPSU membrane made of 17 wt% polymer con-
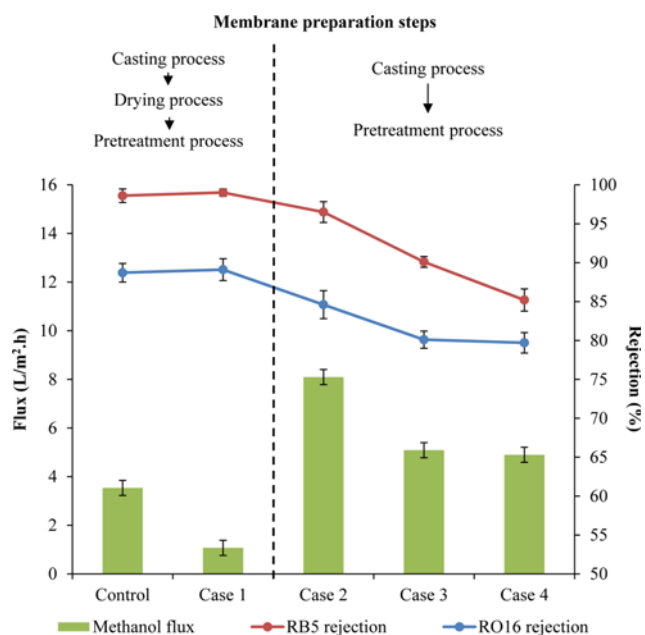
centration for its highest methanol permeability coupled with reasonable rejection capability. The membrane is first pretreated with pure methanol by immersing it into the solution at different immersion periods. The filtration experiment for the membrane pretreated with different conditions was carried out at 6 bar after the membrane is subjected to compaction process at 7 bar for 1 h.

The effect of membrane pretreatment on the membrane performance was carried out using pure methanol and methanol containing two different dyes, RO16 and RB5. The performance of the control membranes is used as reference. The effect of solvent treatment on the methanol flux of PPSU membrane is presented in Fig. 8. As shown, fluxes of methanol are significantly changed when the PPSU membranes are pretreated with methanol. Case 2 had a methanol flux as high as 8.10 L/m²·h, which is >2 times higher than the flux of non-treated membrane. The methanol flux is in the order of case 2 (8.10 L/m²·h)>case 3 (5.09 L/m²·h)>case 4 (4.90 L/m²·h)> case 1 (1.07 L/m²·h). Longer period of immersion causes the membranes to have lower methanol flux. The methanol flux is decreased by approximately 40% after 14 days of immersion. The membranes that go through a drying process after casting have shown to have lower flux as compared to the membrane that directly pretreated in methanol. This is due to the shrinkage of membrane pore during air-drying process. Also, drying the membrane before pretreatment (case 1) caused the membrane to loss even more flux due to permanent pore shrinkage.

Rejection of RB5 and RO16 in methanol with initial concentration of 10 mg/L is also shown in Fig. 8. The rejection of dye is measured to evaluate the effect of the pretreatment process on membrane pore structure. The highest rejection of dyes is achieved by the case 1 membrane, recording as high as 99.0% and 89.1% rejection for RB5 and RO16, respectively. The rejection for both dyes is
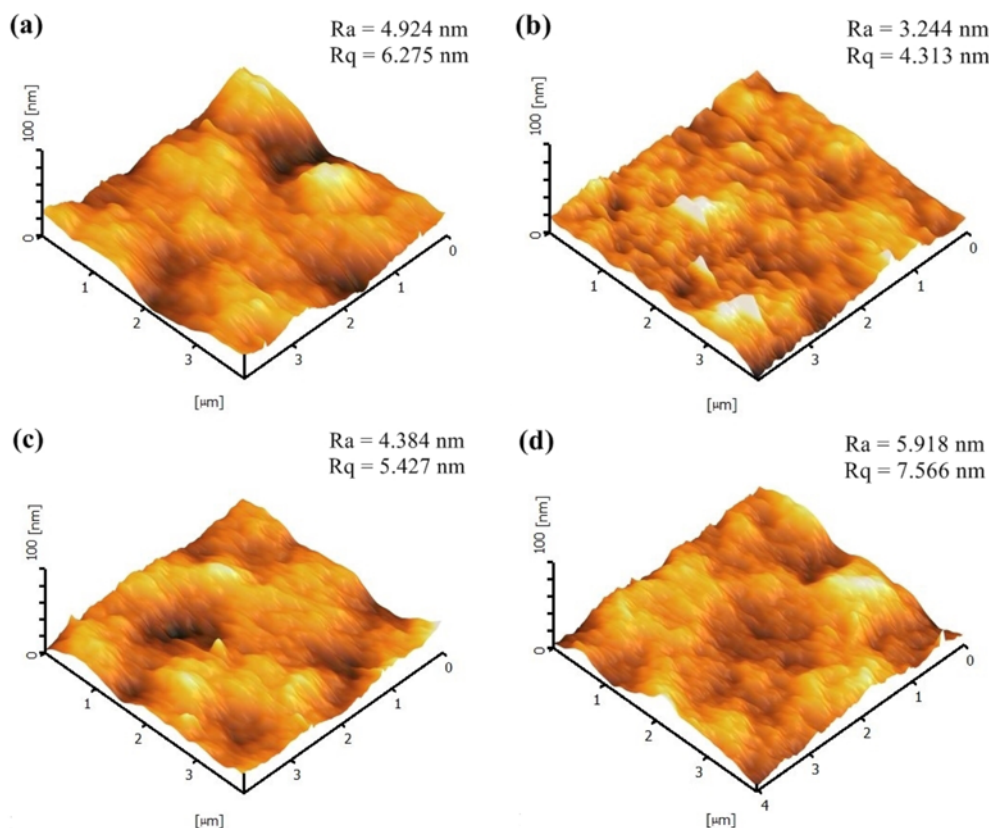
Fig. 9. AFM images of methanol-treated membranes at different pretreatment condition: (a) Case 1, (b) Case 2, (c) Case 3 and (d) Case 4.

reported to decrease in the order of case 1>case 2>case 3>case 4. The results show that the membranes directly immersed in methanol after the casting process have larger pore sizes compared to the pre-dried membranes. The rejection of both dyes decreases with longer immersion period from 96.5% to 85.3% and 84.6% to 79.7% for RB5 and RO16, respectively. These results are supported by the AFM images and roughness of the membranes shown in Fig. 9. The increase of up to 45% of the mean roughness indicates an increase in the pretreated membrane pore size. The reorganization of the membrane internal matrix (due to swelling) after exposing to methanol solvent might have affected the pore size, which changes the membrane's performance.

Although swelling could explain the decline in dye rejection, it does not fit in to describing the decrease in methanol flux through the pretreated membrane. Another possibility is that the membrane surface hydrophilicity might have changed after the membrane was in contact with the methanol [41]. The results show that the surface hydrophilicity may have more prominent effects on the methanol flux than the swelling behavior of the membrane. Considering cases 2, 3 and 4, the decrease in flux after methanol pretreated membranes might be due to the 'clustering effect'. After pretreatment with methanol, a membrane with hydrophilic properties initially becomes slightly hydrophobic [18]. PPSU membrane is semi-hydrophilic, which becomes slightly hydrophobic after methanol pretreatment, resulting in reduced methanol flux. The contact angle value of PPSU membrane after the pretreatment is slightly increased from 69.4° to 70.6° (Table 3). The contact angle measurements on

Table 3. Water contact angles (with standard deviation) of membranes pre-treated by methanol at different durations

Sample	Contact angle (°)
Control	63.9±1.7
Case 1	64.0±1.2
Case 2	69.4±1.6
Case 3	70.4±1.9
Case 4	70.6±1.2

non-treated and pretreated membranes show that methanol decreases the membrane hydrophilicity and negatively affects methanol flux.

For solvent-treated membranes, changes in membrane performance either in the permeability or in the dye rejection are a sign for the influence of organic solvents in the membranes. The pretreatment process might result in increased polymer chain mobility, a characteristic of swollen polymer systems that may be responsible for alterations in the membrane morphology. During the pretreatment process, the membrane active layer is rapidly wetted and curled inward and no apparent dissolution of the membrane structure is observed after the process. FTIR analysis was used to track the changes in the polymer's chemical structure before and after the pretreatment process and the results are shown in Fig. 10. No trace of changes is observed in the membranes' functional groups before and after different pretreatment process. All the IR spectra show characteristic peaks assigned to S=O stretching at $1,165.0\,cm^{-1}$, C-O bending at $1,237.5\,cm^{-1}$ and C=C at $1,485.5\,cm^{-1}$. This indi-
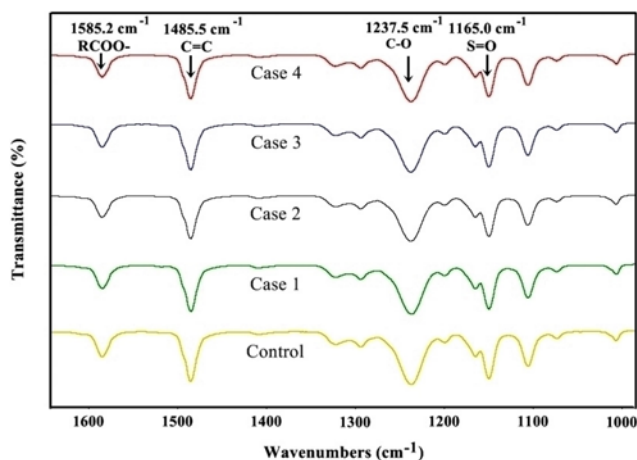
Fig. 10. FTIR spectra for non-treated and pretreated PPSU membranes.

cates that the chemical structure of the membranes is not affected by the different pretreatment conditions.

CONCLUSIONS

The effects of two parameters, polymer concentration and membrane pretreatment condition on final morphology and properties as well as performance of the membranes, were investigated. Results show that with increasing polymer concentration in the polymer dope solution, the number of macrovoids in resulting membrane decreases and their shape changes from finger-like to pear-like structure. Furthermore, the polymer concentration significantly alters the MWCO of the membrane in which increase in the polymer concentration leads to lower MWCO. Regarding the membrane pretreatment conditions, increasing the membrane pretreatment time before testing leads to decrease in the methanol flux and lower rejections. This indicates that the performance of the membrane is affected by the solvent-membrane interactions and membrane swelling. However, the solvent-membrane interactions showed more prominent effects by changing the hydrophilicity of the membranes. The hydrophilicity of the control PPSU membrane was reduced (increased contact angle value) after being pre-treated with methanol solution. Although membrane pretreatment process did alter membrane structural and separation properties, the functional groups of PPSU membrane remained unchanged.

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