



Research Paper

Separation Efficiency of Epoxified-Polyethersulfone Blend Membrane for Chromium Removal

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HIGHLIGHTS

- Prepared (DGEBA–PES) blend membrane through the combined dry-wet phase inversion
- Study of membrane morphology at different exposure duration in dry phase inversion
- Reduce membrane fouling propensity by blending hydrophilic DFEBA with PES polymer
- Role of hydrophilic DGEBA to improve cross-flow filtration and removal of Cr (VI)

ABSTRACT

A microporous bisphenol A diglycidyl ether (DGEBA) epoxified-polyethersulfone (PES) blend membrane (EPES membrane) was prepared through dry-wet phase inversion. This study attempts to correlate the changes in membrane physical and chemical properties when the EPES membranes were exposed to different durations of dry-phase inversion, towards the separation efficiency of carcinogen chromium (VI). Field emission scanning electron microscopy (FESEM) and porometer analysis revealed a small but not significant change of the physical structures of the EPES membranes at different durations of dry-phase inversion that are applied. On the other hand, in terms of chemical properties, both Fourier transform infrared spectroscopy and contact angle measurement demonstrated enhanced membrane hydrophilicity when a longer period of dry phase inversion was imposed during membrane synthesis. The EPES membrane synthesized through 1 h of dry phase inversion showed the most balanced high rejection and permeation performances at $88.84 \pm 0.18\%$ removal of Cr (VI) ions with minimum membrane fouling at a steady permeation flux of 11.27 ± 0.35 L/m²h. From the result, EPES blend membranes revealed good potential in the removal of carcinogen Cr (VI) without jeopardizing the membrane permeation flux.

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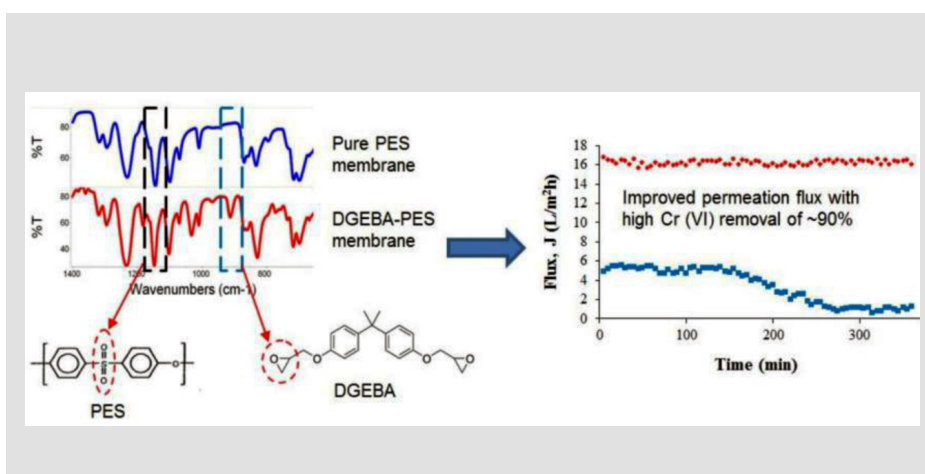
1. Introduction

Industries such as metal plating, mining operations, fertilizer, tanneries, batteries, paper and pesticide manufacturers have heavily discharged of toxic and carcinogenic heavy metals into the environment [1]. Toxic heavy metals of particular concern in the treatment of industrial wastewaters include Zn, Cu, Ni, Hg, Cd, Pb and Cr. Some of these heavy metals are highly soluble in water, making it tend towards accumulating in the environment [2, 3]. Indeed,

excessive concentrations of the heavy metals are detrimental; in turn, all living organisms within a given ecosystem are variously contaminated along their cycles of the food chain.

A lot of methods have been proposed to remove heavy metals from water sources, including but not limited to, chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulation and flocculation, flotation and electrochemical treatment technologies [1, 3-5]. Among these methods,

GRAPHICAL ABSTRACT



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membrane technologies have been chosen because of their simple, advanced and cost-effective way of separation [1, 2]. Polyethersulfone (PES) polymer is one type of dominating material in membrane separation that displays an outstanding chemical and thermal stability, hydrolytic stability as well as high mechanical strength [6–8]. However, PES is also known for its hydrophobic property that leads to serious membrane fouling [8]. Membrane hydrophilicity plays an important role in increasing the permeation flux and selectivity of a separation process. Higher membrane hydrophilicity allows more water molecules to pass through the barrier and renders higher permeate flux [9].

Bisphenol A diglycidyl ether (DGEBA) is a type of polymer resin that contains high concentration of epoxy group, which is widely used in various applications such as coating, adhesives, casting, molding and composite materials. The high porosity, hydrophilicity, good resilience character and abrasion resistance of the DGEBA make it possible to be incorporated into the polymer matrix in order to enhance hydrophilicity of the resultant blend membrane [10]. In the work carried out by Jayalakshmi and co-workers [11], the cellulose acetate-DGEBA blend ultrafiltration membrane was prepared for the removal of Cr ions. The epoxy-functionalized cellulose acetate membrane showed a great improvement in overall membrane hydrophilicity with higher fouling resistance and better separation efficiency [11].

Nevertheless, the use of the additive (DGEBA epoxy resin) in a more complex polymer matrix will change the phase equilibrium and overall mass transfer rate. Therefore, further investigation into membrane phase inversion is needed to control the final membrane morphology and properties. The combined dry and wet phase inversion technique has been discussed by numerous researchers for slower mass transfer processes [12, 13]. The slower mass transfer during dry phase inversion is anticipated to increase compatibility between epoxy DGEBA and PES polymer prior to immersion in a liquid coagulation bath (wet phase inversion).

In this study, we intend to increase hydrophilicity of the PES membrane by integrating hydrophilic DGEBA within the polymer matrix. A series of DGEBA-PES blend membranes were prepared through dry-wet phase inversion, considering different exposure durations in dry-phase inversion. Physical microstructure and chemical properties of the DGEBA-PES blend membrane were further related to its performances in terms of cross-flow filtration and rejection of Cr ions.

2. Materials and methods

2.1. Chemicals and materials

Polyethersulfone polymer (PES, Ultrason E6020P, and MW 58,000 Da) was supplied by BASF (Germany). 1-Methyl 2-pyrrolidone (NMP) was used as solvent to dissolve PES polymer and the epoxy resin, Bisphenol A diglycidyl ether (DGEBA), were purchased from Sigma-Aldrich (Switzerland). The feed Cr solution was prepared using potassium dichromate supplied by Sigma-Aldrich (Switzerland). Reagents used to detect Cr concentration (Acid Reagent Powder Pillows, ChromaVer® 3 Chromium Reagent Powder Pillows, Chromium Reagent Powder Pillows) were purchased from Arachem (Malaysia).

2.2. Membrane preparation

Casting dope was prepared by dissolving 18 wt. % of PES polymer in 82 wt. % of NMP solvent and stirred for 5 h at 25°C. 30 wt. % of DGEBA relative to the weight of the PES polymer was then added to the PES/NMP mixture and the stirring process was continued for 3 h until a homogenous solution was obtained. For example, 18 g of PES polymer was first dissolved in 82 g of NMP solvent. An amount of $18 \times 0.3 = 5.4$ g of DGEBA was then added into the mixture, rendered to a dope weight of 105.4 g. Prior to membrane casting, the dope solution was degassed to eliminate the possible trapped air bubbles. A film applicator (Elcometer 4340, Germany) was used for membrane casting. Dope solution was cast onto a glass plate using the stainless steel casting blade adjusted to 250 μm clearance gap. The solution cast-film was then exposed to dry phase inversion at a controlled humidity at round 55% for a preset exposure time (20 min, 40 min, 1 h, and 1 day), as the membranes' id were designated in Table 1. Subsequently, the cast-film was immersed in a coagulation bath (distilled water) at a temperature of 25°C for 24 h to further induce wet phase inversion to remove the residual solvent.

2.3. Evaluate physical microstructure and chemical properties of the EPES membrane

The surface and cross-sectional morphology of the membranes were visualized using field emission scanning electron microscopy (FESEM, SUPRA TM 35vp Zeiss) at an accelerating voltage of 5 kV. For cross-

sectional analysis, the membranes were fractured using liquid nitrogen. All membrane samples were first coated with platinum (Pt) to prevent surface charges. Meanwhile, the mean through pore diameter and the pore size distribution of the membrane were determined using a liquid-liquid displacement porometer (Porolux 1000, Germany). The membrane sample was first wetted using the perfluoroether (porefill liquid) with a surface tension of 16 dynes/cm. The gas flow (Nitrogen, N_2) was measured as a function of the transmembrane pressure, first through the wet membrane with perfluoroether (wet curve) and then through the dry membrane (dry curve) [14, 15]. During measurement, the pressure of N_2 gas was increased gradually, until all wetting liquid was purged out from the membrane sample. The relationship between the pore size and the corresponding pressure was calculated based on the Young-Laplace equation.

As for chemical properties of the membrane, the presence of DGEBA within the membrane matrix was analyzed using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, NICOLET iS10, USA). Each spectrum was obtained from 32 scans at a 45° incident angle using a diamond crystal over the wavenumber range of 4000–600 cm^{-1} .

Table 1
EPES membrane composition and preparation conditions.

| Membrane id | PES/NMP Composition (wt. %) | | wt. % of DGEBA relative to the weight of PES | Dry phase exposure period |
|-------------|-----------------------------|-----|--|---------------------------|
| | PES | NMP | | |
| EPES-20min | 18 | 82 | 30 | 20 min |
| EPES-40min | 18 | 82 | 30 | 40 min |
| EPES-1h | 18 | 82 | 30 | 1 h |
| EPES-1day | 18 | 82 | 30 | 1 day |

2.4. Membrane performance test

An in-house fabricated cross-flow filtration membrane separation rig was designed and used to perform the separation of Cr from the feed solution with a cell internal diameter of 49 mm and effective membrane area of 18.86 cm^2 . 1 mg/L of Cr solution was used as the feed solution. First, nitrogen gas was used to pressurize the membrane at 7 bar for 30 min to ensure membrane compaction. The feed tank was initially filled with deionized water. The pure water flux (J_0) was measured at a function of time at a constant low pressure of 3 bar until a quasi-steady flux was achieved (usually within 30 min). The feed tank was then replaced by the Cr solution and the cross-flow filtration study was performed at a pressure of 3 bar for 6 h. The accumulated permeate mass which will be used to calculate the filtration flux (J , $\text{L}/\text{m}^2\cdot\text{h}$) was recorded by a computer-recorded electronic balance (FX3000i AND, USA) at an interval time of 5 min. The concentrations of Cr obtained from the accumulated permeate were then measured using DR 5000 Hach Spectrophotometer (USA).

3. Results and discussion

The existence of DGEBA in DGEBA-PES blended membranes were investigated by the ATR-FTIR technique. As shown in Figure 1, pure PES and EPES membranes (20 min, 40 min, 1 h and 1 day) have demonstrated a sharp peak at 1148 cm^{-1} , due to the stretching frequency of S=O bonding (sulfone functional group) of the PES polymer [16]. In addition to the S=O bonding, both pure PES and EPES membranes also show a sharp peak at 830 cm^{-1} , representing the complex aromatic 1, 4 substitution ring (appeared in both PES and EPES membranes) and the C-O-C oxirane (appeared in EPES membrane) [17, 18]. Meanwhile, the spectrum of EPES blend membranes have also revealed a sharp peak at 914 cm^{-1} , due to the C-O-C bonding of the epoxy group (characteristic oxirane ring vibration) [19, 20], as well as demonstrating a peak at 1030 cm^{-1} , which corresponded to the symmetric vibration of the C-O-C alkyl acrylic ether bond [21] existing in the DGEBA resin. Both peaks indicate the successful integration of the DGEBA resin into the PES polymer matrix [10].

It is worth noting that an increase in absorbance intensity of C-O-C bonds in the EPES blend membranes (Figure 1) were observed when the membranes were exposed to a longer duration in dry phase inversion. In Figure 1, the blend EPES membrane that was exposed to 1 day of dry phase inversion indicated having the highest C-O-C epoxy ring absorbance intensity (914 cm^{-1}), C-O-C alkyl acrylic ether bond (1030 cm^{-1}) as well as the

absorbance intensity at 830 cm^{-1} (complex aromatic 1, 4 substitution ring and the C-O-C oxirane).

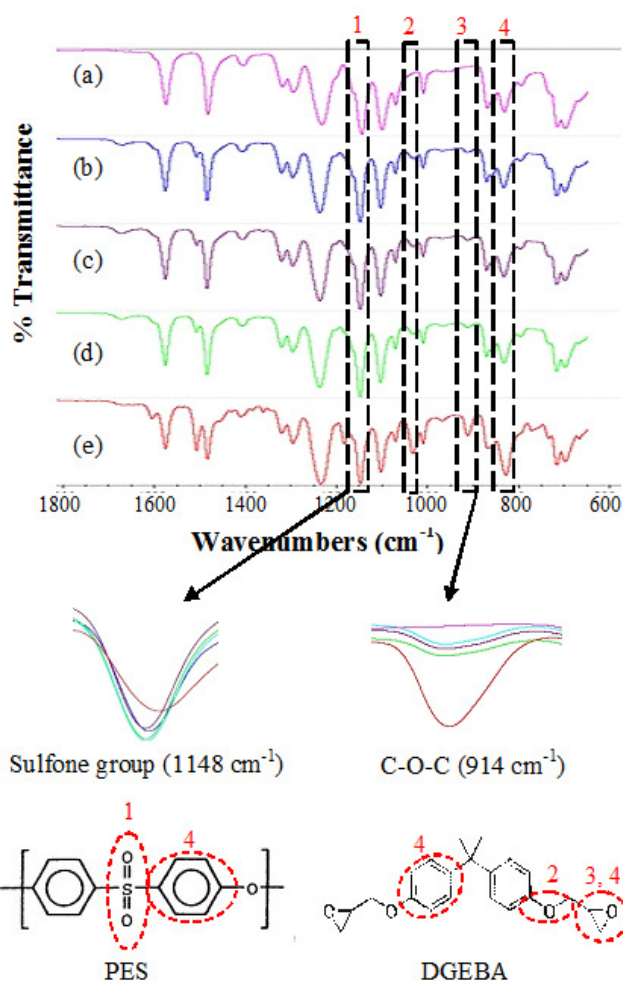


Fig. 1. FTIR spectra of (a) pure PES polymer and DGEBA–PES membranes prepared at: (b) 20 min, (c) 40 min, (d) 1 h, (e) 1 day.

In the present work, all blended EPES membranes were prepared using the same dope formulation (same amount of DGEBA in the casting dope), thus, a similar absorbance intensity of DGEBA C-O-C peaks is anticipated. However, the difference of the C-O-C related absorbance intensities at 914 cm^{-1} (epoxy ring), 1030 cm^{-1} (alkyl acrylic ether bond) and 830 cm^{-1} (oxirane ring) observed in Figure 1 could be related to the mass transfer process during phase inversion. When the longer dry phase inversion took place (20 min to 1 day), the blended DGEBA resin had a higher opportunity to entrap within the partial solidified PES matrix. Throughout subsequent wet-phase inversion, the DGEBA was not easy to leach-out from the cast-film. Thus, it contributed to higher concentration of DGEBA molecules entrapped within the PES membrane (Figure 1e). In contrast, when the blend EPES film was exposed to a short duration of dry phase inversion (20 min, Figure 1b), the DGEBA resin was not able to “lock” firmly within the EPES cast-film. During wet phase immersion precipitation, the high diffusion rate of the non-solvent (deionized water) diffused into the liquid film will eventually flush-out some of the DGEBA resin together with the NMP solvent. Hence, lower peak intensity was observed (Figure 1b), which was found similar to the neat PES membrane (Figure 1a). The higher amount of DGEBA entrapped within the membrane is expected to have better hydrophilic properties that may contribute to higher permeate flux [10].

Figure 2 demonstrates surface and cross-sectional morphologies of EPES membranes prepared at different exposure durations of the dry inversion phase (20 min, 40 min, 1 h and 1 day). As shown in the FESEM micrographs, they were slightly different on the surface of the blend membranes, while cross-sectional pore structures for all EPES membranes were found almost similar (Figure 2). Under the perspective of the membrane sieving mechanism, it is presumed that the EPES membranes will have similar separation performances, in both permeation flux and Cr selectivity. Indeed,

the similarity of the membrane physical microstructures was due to the same dope formulation that was used to cast the membranes (18 wt. % of PES polymer and 30 wt. % of DGEBA resin). In addition, similar membrane preparation procedures were adopted except the different exposure duration during dry phase inversion.

In fact, in the present work, membrane solidification was dominated by the wet-phase immersion precipitation. The dry phase inversion was not able to completely solidify the PES. Up to an hour of dry-phase inversion, only slight opaque areas were spotted throughout the cast-film. The dry phase inversion could only turn a partial of the membrane into thermodynamically unstable (merely partial opaque areas were spotted), due to the low volatility of the NMP solvent that causes slower evaporation of the solvent (NMP) than the intake of non-solvent (water vapor) into the cast-film [22]. Thus, the demixing process for the formation of membranes was slightly delayed. Some NMP solvents still remained within the cast-film and existed as a “gel” state. Indeed, this slow precipitation rate (delayed demixing) assists in producing the sponge-like structure [23].

In the present work, the complete solidification was dominated by the latter wet-phase immersion precipitation, with all NMP solvents diffused out from the membrane by the non-solvent (deionized water in the coagulation bath). Thus, similar physical membrane microstructures were formed, as shown in Figure 2. The only observable different morphologies were about the gap between the membrane pores. From Figure 2, both EPES membranes exposed to 1 h and 1 day of dry phase inversion exhibited a closer membrane pores’ gap (distance between the individual pores). Meanwhile, the membrane with 20 min of dry phase inversion showed a relatively bigger pore gap. As mentioned before, a slow demixing process occurred during dry phase inversion, leading to the formation of a microporous structure on the membrane surface when more DGEBA was entrapped within the polymer matrix. Hence, a longer period of dry phase inversion enables more pores to form on the surface of the blend membranes. However, the differences between the pore gaps were small and not significant (Figure 2). Therefore, the membrane physical morphology is believed to have only a minor effect on the final membrane separation performances.

The cross-sectional structures (Figure 2) of all EPES membranes showed homogeneous porous structure on the top region of the membrane cross-section and some small macrovoids were observed at the bottom cross-sectional region of the membrane. During dry phase inversion, DGEBA was entrapped within the polymer matrix. Dry phase inversion was a slow demixing process; therefore, the top region of the cast film becomes a polymer-rich phase while the bottom region of the membrane was a polymer-lean phase. Since DGEBA resin is a light phase molecule, after a certain period of dry phase inversion, some DGEBA molecules stood a higher chance to settle down at the bottom region of the film prior to getting subjected to the rapid wet phase immersion precipitation [24]. As discussed earlier in Figure 1, the cast film was fully solidified in the latter wet-phase inversion with some DGEBA molecules that were flush-out from the polymer matrix. Consequently, the polymer-lean phase at the bottom region of the cast film will eventually create macrovoids in the latter wet phase inversion as the DGEBA molecules were flush-out from the polymer matrix. Furthermore, when a higher amount of hydrophilic DGEBA was entrapped within the polymer matrix (1 day of dry phase inversion), the hydrophilic DGEBA molecules will attract more non-solvent (water molecules in the coagulation bath) diffusion into the membrane forming film. This process increased the thermodynamic instability of the polymer solution when reacted with water, which could cause a rapid phase demixing and then lead to the formation of a big porous structure (small macrovoids) at the bottom region of the membrane [25]. However, since the same dope formulations were used for all EPES membranes, the physical cross-section of the polymers were found to be similar.

Figure 3 represents the wet and dry curves of the EPES membranes, analyzed using the liquid–liquid displacement porosimeter. At a specific pressure, the total gas-flow through a wet sample is always smaller than that through the corresponding dry sample until the two curves meet together, where all wetting liquid in the membrane pores are purged out from the sample [26]. In the previous work, the effectiveness of the EPES membrane was proven by comparing it to the neat PES membrane [10]. Thus, the present work only focused on the EPES membranes that were prepared under different exposure durations to the dry phase inversion. Based on Figure 3, EPES membranes exposed to 20 min (Figure 3a) and 1 day (Figure 3d) of dry phase inversion demonstrated the lowest and highest pressure that needs to purge all of the wetting liquid from the membrane pores, which is 6.6 bar and 9.8 bar, respectively. The EPES membrane that was exposed to 1 day of dry phase inversion contained a relatively closer pores’ gap, as demonstrated in Figure 2d, which was technically rendered to a higher pores density or the membrane may consist of higher quantities of small pores, and thus needs higher pressure to purge out all the wetting liquid.

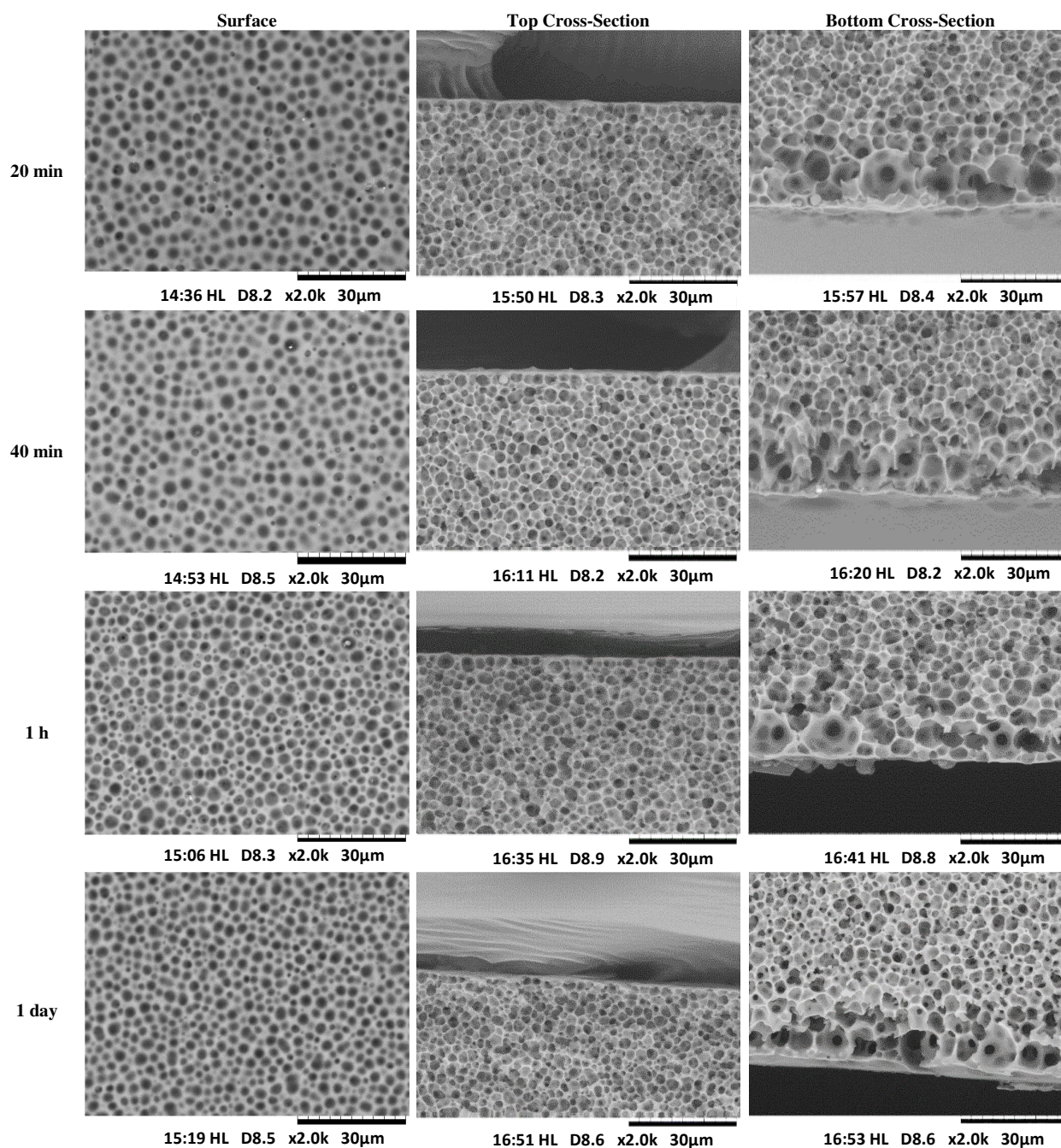


Fig. 2. FESEM micrographs for surface and cross-sectional of DGEBA-PES membranes.

Table 2 summarized the mean pore sizes and porosities for EPES blend membranes prepared at different exposure time in the dry phase inversion, calculated based on the Young-Laplace equation and analyses from the liquid-liquid displacement porometer as well as the porosity measurement, respectively. The membrane pores were calculated at 0.104 μm , 0.097 μm , 0.117 μm and 0.133 μm , for EPES-20min, EPES-40min, EPES-1h and EPES-1day, respectively. As demonstrated in Figure 3, areas in between the dry and wet curves were found larger for membranes EPES-1h and EPES-1day. This reflects the higher amount of porefill liquid (wetting liquid used for pore size measurement) filled within the polymer matrix; thus, rendering slightly bigger measured mean pore sizes as 0.1166 μm and 0.1334 μm in Table 2. Whilst, all membrane porosities fell around 71.5-73.5%. Generally, the mean pore sizes and the membrane porosities did not differ much amongst each other. Hence, these results were still in-line with the qualitative ones observed from FESEM images (Figure 2), where the EPES blend membranes does not differ much in terms of its physical pore structures.

Adding the hydrophilic DGEBA resin into a hydrophobic PES casting dope can make the resultant membrane suitable for water treatment

processing, improving water permeability and reducing fouling propensity. The EPES blend membranes hydrophilicity levels were measured based on the contact angle analyses and data were tabulated in Table 2. The lowest contact angle of 51.8° was found when the membrane was exposed to 1 day of dry-phase inversion. As discussed earlier, a longer exposure period in the dry phase inversion would help to entrap more hydrophilic DGEBA resin within the polymer matrix, and thus improved the membrane hydrophilicity. Indirectly, the longer exposed duration in dry phase inversion contributes to better membrane hydrophilicity properties. With improved membrane hydrophilicity, higher permeation and lower fouling propensity are anticipated throughout the filtration processes.

Figure 4 demonstrates the cross-flow filtration performances of the EPES blend membranes. 1 ppm of Cr solution mixed with 1wt. % of polyethyleneimine (PEI) was used as the feed solution. It has been generally accepted that membrane productivity is closely related to the membrane pore size [27]. However, in Figure 4, the result seems to be counterintuitive as, in general, the membrane physical microstructures were found almost similar amongst each other (Figure 2 and Table 2), hence; the membrane permeations are expected to be comparable. However, in Figure 4, the EPES membrane

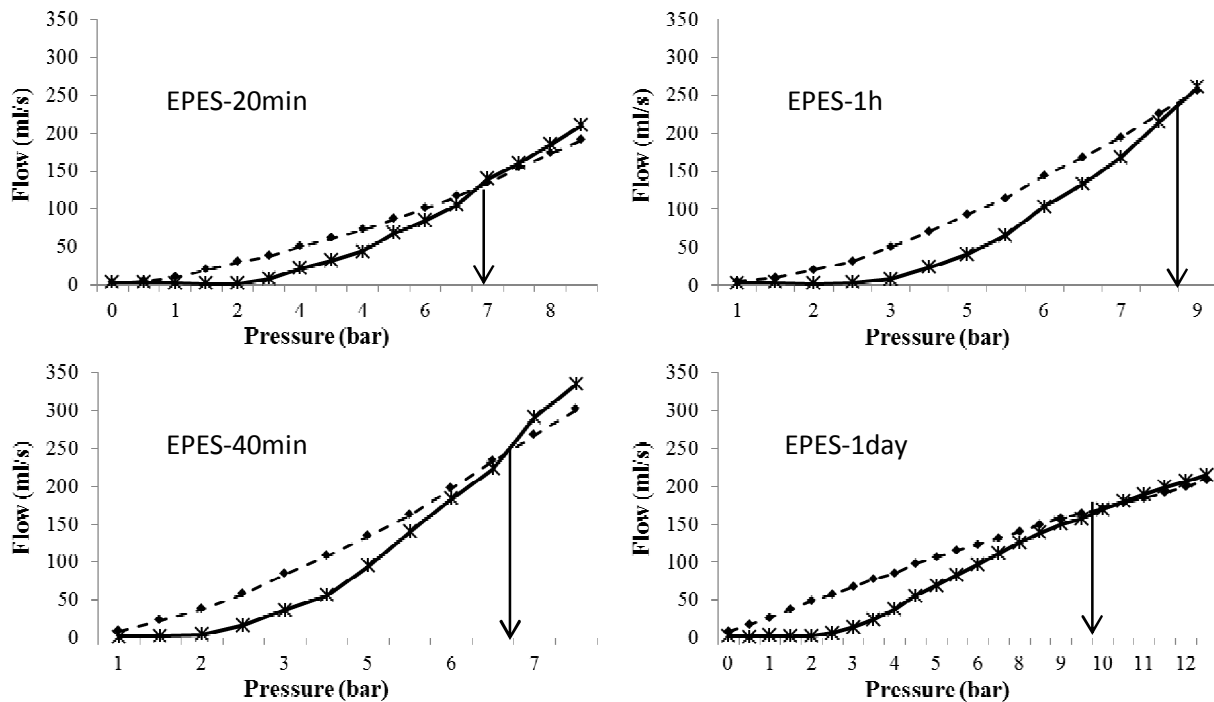


Fig. 3. Wet and dry curve for DGEBA–PES blend membranes (dotted line: dry curve; solid line: wet curve).

Table 2
Mean pore size and contact angle measurement for EPES blend membranes.

| DGEBA–PES Membrane | Mean pore size (μm) | Contact angle (θ°) | Porosity (%) |
|--------------------|---------------------|--------------------|--------------|
| EPES-20min | 0.104 ± 0.007 | 68.2 ± 0.2 | 72.7 ± 0.7 |
| EPES-40min | 0.097 ± 0.003 | 62.8 ± 0.6 | 73.5 ± 0.8 |
| EPES-1h | 0.117 ± 0.021 | 54.3 ± 0.3 | 73.2 ± 0.2 |
| EPES-1day | 0.133 ± 0.015 | 51.8 ± 0.3 | 71.5 ± 0.6 |

exposed to 1 day of dry phase inversion has demonstrated the highest permeation at $16.22 \pm 0.23 \text{ L/m}^2\text{h}$, while the membrane prepared under 20 min of dry phase inversion showed the lowest flux at $5.17 \pm 0.26 \text{ L/m}^2\text{h}$.

In the present work, membrane permeation was dominantly affected by the chemical properties; i.e. the higher membrane hydrophilicity achieved by the addition of the DGEBA which eventually plays an important role in affecting the overall permeation performances (Figure 4 and Table 3). By using EPES-20 min as the control membrane, the initial flux performed by the control membrane (EPES-20min) was shown to have permeation around 5.17

$\pm 0.26 \text{ L/m}^2\text{h}$, indicating the lowest flux. After 3 h of filtration, fluxes reduced and become steady. The permeate flux for the EPES-20min membrane has dropped to $1.21 \pm 0.14 \text{ L/m}^2\text{h}$. Indeed, this flux was too low and not applicable for industrial applications. Compared to the control membrane (EPES-20min), the steady state membranes' fluxes were increased to 326%, 838% and 1239% for EPES membranes prepared by exposing the membrane to 40 min, 1h and 1 day in dry phase inversion, respectively, as tabulated in Table 3. These values show the capability of DGEBA to enhance the membrane hydrophilicity and further increased the permeation flux [11]. The EPES membrane prepared under 1 day exposure in dry phase inversion (EPES-1day) contained the highest amount of DGEBA which translates to better hydrophilic properties. The improvement on the membrane hydrophilicity inhibits the existing interactions between solute and membrane surface [23], hence, creating lower diffusion resistance for water molecules to permeate across the membrane. Moreover, the hydrophilic DGEBA-PES membrane has also shown successfully suppressed membrane fouling, with small but not significant fouling that was found in the EPES-1day membrane. The observed improvement of antifouling properties for the DGEBA-PES blend membrane was attributed to the hydrophilic property of the epoxy resin [28]. By its outstanding flux, the EPES membrane prepared under 1 day of phase inversion is supposed to be the best performing membrane in the present work.

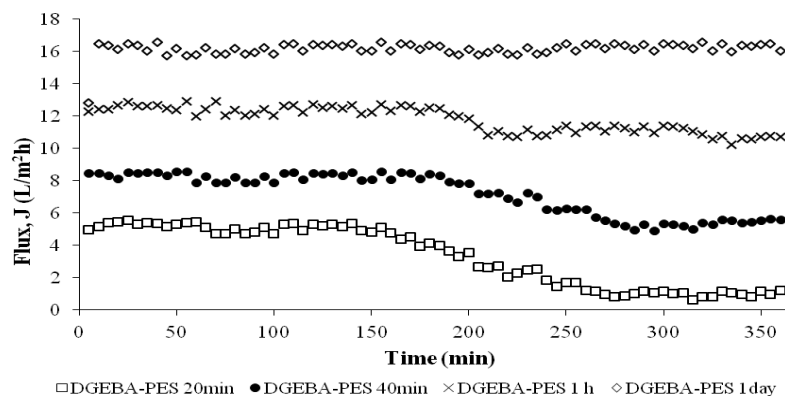


Fig. 4. Flux for filtration of EPES membrane.

Table 3

Initial and steady flux for membrane prepared at different duration of dry phase inversion

| DGEBA-PES Membrane | Initial flux (L/m ² h) | Improved flux (%) | Steady flux (L/m ² h) | Improved steady flux (%) |
|--------------------|-----------------------------------|-------------------|----------------------------------|--------------------------|
| EPES-20min * | 5.17 ± 0.26 | - | 1.21 ± 0.14 | - |
| EPES-40min | 8.18 ± 0.25 | +60 | 5.09 ± 0.30 | +326 |
| EPES-1h | 12.10 ± 0.27 | +137 | 11.27 ± 0.35 | +838 |
| EPES-1day | 16.22 ± 0.23 | +217 | 16.04 ± 0.33 | +1239 |

* DGEBA-PES Membrane exposed to 20 min of dry phase inversion was acted as the control membrane to evaluate membrane permeability.

The chromium rejection performances of DGEBA–PES membranes are shown in Table 4. The EPES blend membrane that was exposed to 40 min of dry phase inversion showed the highest rejection of Cr ion amongst the membranes which is 96.46 ± 0.19 % of the total Cr. Overall, all EPES membranes have performed high total Cr rejection. When monitored closely (Table 4), membranes prepared with 20 min and 40 min of dry phase inversion (EPES-20min and EPES-40min) have also demonstrated relatively high Cr (VI) rejection. However, when it comes to the Cr rejection, the EPES-1day membrane had the lowest percentage of Cr (VI) rejection (80.75 ± 0.26 %). Compared to the control membrane (EPES-20min), 12.41 % reduction of Cr (VI) was found when the membrane was prepared under 1 day of dry phase inversion. Indeed, the membrane prepared at a longer duration of dry phase inversion should have better Cr (VI) rejection since it contained the highest DGEBA resin that chemically attracts (carboxyl group) the heavy metals. Unfortunately, the flux solution was too high (16.22 ± 0.23 L/m²h), which is about 217% and 1239% for the initial flux and steady flux, respectively, as compared to the control membrane (EPES-20min membrane). Hence, a portion of the DGEBA molecules were unable to retain the absorbed Cr within the polymer matrix and flush-out. Thus, the EPES-1h membrane was chosen as the best performed membrane in the present work. The DGEBA-PES-1h membrane was able to perform high flux at 12.10 ± 0.27 L/m²h (838 % increase of steady flux) with only a slight reduction of Cr (VI) rejection 88.84 ± 0.18 % (3.64 % lower).

Table 4

Rejection of Cr ions for membrane prepared at different duration of dry phase inversion.

| DGEBA-PES Membrane | Rejection % | | | |
|--------------------|--------------|--------------|--------------|----------------------|
| | Total Cr | Cr(III) | Cr(VI) | Improved Cr (VI) (%) |
| EPES-20min * | 92.10 ± 0.24 | 91.87 ± 0.22 | 92.19 ± 0.17 | - |
| EPES-40min | 96.46 ± 0.19 | 95.78 ± 0.18 | 96.63 ± 0.12 | +4.83 |
| EPES-1h | 84.09 ± 0.23 | 69.62 ± 0.11 | 88.84 ± 0.18 | -3.64 |
| EPES-1day | 73.67 ± 0.16 | 53.85 ± 0.17 | 80.75 ± 0.26 | -12.41 |

* DGEBA-PES Membrane exposed to 20 min of dry phase inversion was acted as the control membrane to evaluate Cr (VI) selectivity performance.

4. Conclusions

This study demonstrates the effect of DGEBA additive to increase the hydrophilicity and Cr ions separation efficiency of the PES membrane. FTIR analysis demonstrates the presence of C–O–C bonding on the EPES membranes, indicating the successful integration of the DGEBA within the polymer matrix. FESEM showed similar membrane physical morphologies among the EPES membranes although the membranes were exposed to different durations in the dry-phase inversions. Due to the increased membrane hydrophilicity proven by the contact angle analysis, the overall permeation flux was enhanced. In the present work, the EPES membrane cast under 1h of dry phase inversion revealed excellent rejection of Cr (VI) ions at 88.84 ± 0.18 % with a high steady permeate flux of 11.27 ± 0.35 L/m²h.

5. Acknowledgements

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6. References

- F.L. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: a review, *J. Environ. Manage.* 92 (2011) 407–18.
- A.E. Pagana, S.D. Sklari, E.S. Kikkinides, V.T. Zaspalis, Combined adsorption–permeation membrane process for the removal of chromium (III) ions from contaminated water, *J. Membr. Sci.* 367 (2011) 319–324.
- A.E. Pagana, S.D. Sklari, E.S. Kikkinides, V.T. Zaspalis, Microporous ceramic membrane technology for the removal of arsenic and chromium ions from contaminated water, *Microporous Mesoporous Mat.* 110 (2008) 150–156.
- M.A. Ahmed, S.M. Ali, S.I. El-Dek, A. Galal, Magnetite–hematite nanoparticles prepared by green methods for heavy metal ions removal from water, *Mater. Sci. Eng. B* 178 (2013) 744–751.
- I. Sheet, A. Kabbani, H. Holail, Removal of heavy metals using nanostructured graphite oxide, silica nanoparticles and silica/graphite oxide composite, *Energy Procedia* 50 (2014) 130–138.
- L.J. Zhu, L.P. Zhu, J.H. Jiang, Z. Yi, Y.F. Zhao, B.K. Zhu, Y.Y. Xu, Hydrophilic and anti-fouling polyethersulfone ultrafiltration membranes with poly(2-hydroxyethyl methacrylate) grafted silica nanoparticles as additive, *J. Membr. Sci.* 451 (2014) 157–168.
- C. Zhao, J. Xue, F. Ran, S. Sun, Modification of polyethersulfone membranes – A review of methods, *Prog. Mater. Sci.* 58 (2013) 76–150.
- P.T.P. Aryanti, S. Subagio, D. Ariono, I.G. Wenten, Fouling and rejection characteristic of humic substances in polysulfone ultrafiltration membrane, *J. Membr. Sci. Res.* 1 (2015) 41–45.
- H.X. Nguyen, B. Van der Bruggen, Nanofiltration of synthetic and industrial dye baths: Influence of temperature on rejection and membrane fouling, *J. Membr. Sci. Res.* 1 (2015) 34–40.
- M.J.J. Erniza, S.C. Low, Chromium (III) Removal by Epoxy-Cross-Linked Polyethersulfone Ultrafiltration Membrane, *Jurnal Teknologi (Sciences & Engineering)* 70 (2014) 19–22.
- A. Jayalakshmi, S. Rajesh, S. Senthilkumar, D. Mohan, Epoxy functionalized poly(ether-sulfone) incorporated cellulose acetate ultrafiltration membrane for the removal of chromium ions, *Sep. Purif. Technol.* 90 (2012) 120–132.
- D. Bouyer, W. Werapun, C. Pochat-Bohatier, A. Deratani, Morphological properties of membranes fabricated by VIPS process using PEI/NMP/water system: SEM analysis and mass transfer modelling, *J. Membr. Sci.* 349 (2010) 97–112.
- P.K. Annamalai, C. Pochat-Bohatier, D. Bouyer, C.L. Li, A. Deratani, D.M. Wang, Kinetics of mass transfer during vapour-induced phase separation (VIPS) process and its influence on poly(vinylidene fluoride) (PVDF) membrane structure and surface morphology, *Desalin. Water Treat.* 34 (2011) 204–210.
- S. Kaur, Z. Ma, R. Gopal, G. Singh, S. Ramakrishna, T. Matsuura, Plasma-induced graft copolymerization of poly(methacrylic acid) on electrospun poly(vinylidene fluoride) nanofiber membrane, *Langmuir* 23 (2007) 13085–13092.
- Y. Fang, H.D. Tolley, M.L. Lee, Simple capillary flow porometer for characterization of capillary columns containing packed and monolithic beds, *J. Chromatogr. A* 1217 (2010) 6405–6412.
- I. Sadeghi, A. Aroujalian, A. Raisi, B. Dabir, M. Fathizadeh, Surface modification of polyethersulfone ultrafiltration membranes by corona air plasma for separation of oil/water emulsions, *J. Membr. Sci.*, 430 (2013) 24–36.
- G. Nikolic, S. Zlatkovic, M. Cakic, S. Cakic, C. Lacnjevac, Z. Rajic, Fast fourier transform IR characterization of epoxy GY systems crosslinked with aliphatic and cycloaliphatic EH polyamine adducts, *Sensors* 10 (2010) 684–696.
- A. Chandramohan, M. Alagar, Synthesis and characterization of 1, 1-bis (3-methyl-4-epoxyphenyl) cyclohexane-toughened DGEBA and TGDDM organo clay hybrid nanocomposites, *High Perform. Polym.* 23 (2011) 197–211.
- N. Goran, Z. Sasa, C. Milorad, C. Suzana, L. Caslav, R. Zoran, Fast Fourier transform IR characterization of epoxy GY systems crosslinked with aliphatic and cycloaliphatic EH polyamine adducts, *Sensors* 10 (2010) 684–696.
- U. Braun, K. Brademann-Jock, W. Stark, Cure monitoring of epoxy films by heatable in situ FTIR analysis: Correlation to composite part, *J. Appl. Polym. Sci.* 131 (2014) DOI:10.1002/app.39832.
- M.G. González, J.C. Cabanelas, J. Baselga, Applications of FTIR on epoxy resins - identification, monitoring the curing process, phase separation and water uptake, in: T. Theophanides (Eds.), *Infrared spectroscopy - Materials Science, Engineering and Technology*, InTech, Croatia, 2012, pp. 261–284.
- Y.S. Su, C.Y. Kuo, D.M. Wang, J.Y. Lai, A. Deratani, C. Pochat, D. Bouyer, Interplay of mass transfer, phase separation, and membrane morphology in vapor-induced phase separation, *J. Membr. Sci.* 338 (2009) 17–28.
- J. García-Ivars, M.I. Iborra-Clar, M.I. Alcaina-Miranda, B. Van der Bruggen, Comparison between hydrophilic and hydrophobic metal nanoparticles on the phase separation phenomena during formation of asymmetric polyethersulphone membranes, *J. Membr. Sci.* 493 (2015) 709–722.
- A.L. Ahmad, S.C. Low, S.R.A. Shukor, Effects of membrane cast thickness on controlling the macrovoid structure in lateral flow nitrocellulose membrane and determination of its characteristics, *Scr. Mater.* 57 (2007) 743–746.

- [25] C. Barth, M.C. Gonçalves, A.T.N. Pires, J. Roeder, B.A. Wolf, Asymmetric polysulfone and polyethersulfone membranes: Effects of thermodynamic conditions during formation on their performance, *J. Membr. Sci.* 169 (2000) 287-299.
- [26] S.C. Low, A.L. Ahmad, N. Ideris, Q.H. Ng, Interaction of isothermal phase inversion and membrane formulation for pathogens detection in water, *Bioresour. Technol.* 113 (2012) 219-224.
- [27] P. Shah, C.N. Murthy, Studies on the porosity control of MWCNT/polysulfone composite membrane and its effect on metal removal, *J. Membr. Sci.* 437 (2013) 90-98.
- [28] S.O. Han, L.T. Drzal, Water absorption effects on hydrophilic polymer matrix of carboxyl functionalized glucose resin and epoxy resin, *Eur. Polym. J.* 39 (2003) 1791-1799.