Role of Graphene Oxide in Support Layer Modification of Thin Film Composite (TFC) Membrane for Forward Osmosis Application

(Peranan Oksida Grafin dalam Pengubahsuaian Lapisan Sokongan Membran Komposit Filem Nipis (TFC) untuk Aplikasi Osmosis ke Hadapan)

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ABSTRACT

In this work, the effect of graphene oxide (GO) incorporation into the membrane support layer towards the performance of thin-film composite (TFC) membrane was investigated. The support layer was fabricated by phase inversion method with the incorporation of GO as hydrophilic nanoparticles. Next, the active polyamide layer was formed on the membrane support layer via interfacial polymerization between trimesoyl chloride (TMC) and m-Phenylenediamine (MPD). The cross-section images from Field-Emission Scanning Electron Microscope (FESEM) showed the presence of active polyamide layer on the surface of TFC membrane while the FTIR results indicated the existence of bands associated with the amide linkages. The initial study showed that an optimal amount of GO (0.5 wt%) incorporation into the polymer substrate resulted in favourable improvement in TFC membrane performance. The physical and chemical properties of GO helps in enhancing the water transport through the membrane polymer matrix and thus contributing to higher permeate flux. The TFC-FO membrane incorporated with GO showed 44% improvement in terms of water flux (3.72 compared to 2.09 Lm^{-2} h^{-1} for pure PSf membrane) and minimal improvement in reverse solute diffusion (0.02 compared to 0.03 g m^{-2} h^{-1} for pure PSf membrane). Thus, this study showed that small addition of GO nanoparticles into the membrane support layer leads to an increase in performance of TFC membrane for FO application.

Keywords: Graphene Oxide; Support Layer; Water Permeation; Thin Film Composite; Forward Osmosis

ABSTRAK

Kajian ini membentangkan kesan penambahan oksida grafin ke dalam lapisan sokongan membran terhadap prestasi membran komposit filem nipis. Lapisan sokongan membran komposit filem nipis dihasilkan melalui teknik fasa songsang dengan penambahan nanopartikel oksida grafin sebagai nanopartikel bersifat hidrofilik. Seterusnya, lapisan aktif poliamida dihasilkan di atas permukaan lapisan sokongan membran dengan kaedah pempolimeran antara muka menggunakan bahan kimia trimesil klorida dan m-Fenilenediamina. Imej keratan rentas dari FESEM membuktikan kehadiran lapisan aktif poliamida di atas permukaan lapisan sokongan membran komposit filem nipis manakala keputusan FTIR menunjukkan kehadiran jalur yang dikaitkan dengan jalur amida. Kajian awal menunjukkan bahawa jumlah optimum oksida grafin (0.5 wt%) yang dimasukkan ke dalam substrat polimer menghasilkan peningkatan yang baik terhadap prestasi membran komposit filem nipis. Sifat fizikal dan kimia oksida grafin membantu dalam meningkatkan pengaliran air melalui matriks polimer membran dan seterusnya menyumbang kepada ketelapan air yang tinggi. Membran komposit filem nipis yang telah ditambah oksida grafin menunjukkan peningkatan sebanyak 44% dari segi fluks air (3.72 berbanding dengan 2.09 Lm^{-2} h^{-1} untuk membran polisulfon tulen) dan sedikit peningkatan dalam penyebaran garam berbalik (0.02 berbanding dengan 0.03 g m^{-2} h^{-1} untuk membran polisulfon tulen). Oleh itu, kajian ini menunjukkan bahawa penambahan oksida grafin ke dalam lapisan sokongan membran menyebabkan peningkatan prestasi membran komposit filem nipis untuk kegunaan osmosis ke hadapan.

Kata kunci: Oksida Grafin; Lapisan Sokongan; Ketelapan Air; Komposit Filem Nipis; Osmosis ke Hadapan

INTRODUCTION

Forward osmosis (FO) has been a good alternative to replace the pressure-driven membrane as it offered valuable advantages including low membrane fouling, high rejections to contaminants and low energy consumption. Since FO is driven by only osmotic pressure, the energy cost can be lower due to the absence of external hydraulic pressure (McGinnis & Elimelech 2007). Despite all the great advantages that FO membrane can offer, this process is still facing some challenges that inhibit its widespread application. The major problem is less availability of good membrane with high water permeation and good rejection properties (Qin, Lay & Kekre 2012).

Recently, researchers have focused on fabricating the thin film composite (TFC) membrane as this type of membrane has been reported to have a better performance in FO application as comparison to the cellulose triacetate membrane which is commercially available (Puguan et al. 2014; Wei et al. 2011). TFC membrane has been modified with several methods in which one of the methods has gained much attention among the researchers which is modification of the support layer (Bui, Nhu-ngoc and McCutcheon 2013; Hoover, Schiffman & Elimelech 2013). The support layer of TFC membrane was one of the important parts contributing to the membrane performance as it directly affect the internal concentration polarization (ICP) phenomena in the membrane. The effect of ICP could be tremendous as it could reduce the solute diffusion rate throughout the membrane which in turned decrease the water permeability of the membrane. The support layer could be modified by increasing its porosity and hydrophilicity to mitigate the ICP problem in the membrane as per suggested by (Ma et al. 2013).

Incorporation of nanoparticles into polymeric membrane has gained much attention as one of the ways to enhance the performance of TFC membrane. Titanium dioxide (TiO$_2$) (Emadzadeh et al. 2014) and modified carbon nanotubes (Wang et al. 2013) have been proven to reduce the ICP effect in the membrane which improve the membrane performance. In addition to this, porous zeolite nanoparticles have also being incorporated into the membrane support layer (Ma et al. 2013). One of the nanoparticles that gained much attention in improving the properties of membrane was graphene oxide (GO). This nanoparticle offered high surface area-to-volume ratios which ensure better interaction with polymer matrix as compared to other type of nanoparticles (Stankovich et al. 2006). Up until today, many studies have been conducted on the capability of GO to improve membrane performances. The water flux of polyvinylidene fluoride (PVDF) membrane has been significantly increased after GO incorporation due to the improvement in hydrophilicity of the membrane (Zhao et al. 2013). In another study, it was demonstrated that GO nanoparticles could act as a modifier which not only improve the water flux but also result in increase in antifouling property (Wang et al. 2012). PES/GO membrane was also shown to have higher water permeation and better antifouling properties with GO incorporation compared to the pure PES membrane

(Zinadini et al. 2014). In addition to that, GO had been used in fabricating FO membrane which improve the water permeation and antibacterial properties of the membrane. Several recent works which reported the incorporation of GO including study by Soroush et al. (2015), which covalently bonded GO/Ag nanocomposites to the TFC polyamide membrane surface to produce superhydrophilic membranes whereas Perreault et al. (2016) proved that the biofouling problem in FO membrane had reduced after incorporation of GO into TFC FO membrane by amine coupling reaction. In addition to this, a study reported a polyamide-graphene oxide FO membrane which was fabricated by cross-linking of GO aggregates with m-xylylenediamine (MXDA) and trimethyle chloride (TMC) also exhibited high water flux (Jin et al. 2018).

Eventhough GO has proven to improve the membrane performance including FO membrane, many conducted studies were only focusing on the surface modification of TFC membrane which somehow involves the changes in the polyamide active layer only. Up to date, there was still limited study being done on the support layer modification of TFC membrane by incorporation of GO nanoparticles. Hence, this study was conducted to investigate the role of GO in enhancing the performance of TFC membrane.

METHODOLOGY

MATERIALS

Graphite powder and N,N-Dimethylacetamide (DMAc) were purchased from Merck (Germany) while sulfuric acid (H$_2$SO$_4$) were from Accot (Malaysia). Potassium permanganate (KM$_n$O$_4$), 1,3,5-Benzenetricarbonyl trichloride (TMC) and m-Phenylenediamine (MPD) were obtained from Sigma Aldrich (USA). Polymer, polysulfone (PSf) was from GoodFellow (UK). Hexane and sodium chloride (NaCl) were supplied by R&M (Malaysia). All the solutions were prepared with deionized water (DI).

GO SYNTHESIS

Modified Hummer's Method has been used to synthesis GO in laboratory scale as being described clearly in one of the previous study by (Mahmoudi et al. 2015).

SUPPORT LAYER FABRICATION

Phase inversion technique was devoted to fabricate PSf and PSf/GO by using DMAc as a solvent. PSf was dissolved into the solvent at weight composition of 18:82 respectively as a casting solution. Different wt% of GO with respect to PSf which ranging from 0.1-1.0 wt% were dissolved into the casting solution and was continously stirred at 300 rpm for overnight to form a homogenous solution. Then, the solution was kept unstirred in the dessicator for another overnight. Before fabrication, the casting solution was sonicated for 30 minutes. The casting solution was casted with Elcometer 4340 Automatic Film Applicator available in the laboratory with

the casting thickness of 200 μm. Immediately, the glass plate was immersed horizontally in the ultrapure water after being exposed to air for 15 secs. The membranes fabricated were denoted as pure PSf, PSFGO-0.1, PSfGO-0.25, PSfGO-0.5, PsfGO-0.75 and PSfGO-1.0, according to the amount of GO incorporated into it.

INTERFACIAL POLYMERIZATION OF TFC FO MEMBRANE

The membrane was air-dried for overnight before the procedure was started. The membrane was taped nicely on a glass plate before being immersed for 2 minutes in the 2% MPD solution. Finally, the membrane was immersed in 0.1% TMC/hexane for 1 minute. The membrane was kept in a container filled with DI water for futher testing (Low et al. 2015).

CHARACTERIZATION AND ANALYTICAL METHODS

Functional groups of GO was analyzed by using FTIR spectrometer (Thermo Fisher Scientific Inc., USA) and the crystallinity of GO was tested by XRD (Bruker D8 Advance, Germany). The changes in the morphology of the membrane support layer was viewed by using Field-Emission Scanning Electron Microscope (Gemini model SUPRA 55VP-ZEISS, Germany). The roughness analysis were done by Atomic Force Microscopy (NTEGRA Prima, NT-MDT, Russia). The surface hydrophilicity of membrane support layer were analyzed using a Drop Shape Analysis System goniometer.

WATER PERMEABILITY TEST

Membrane permeability was tested with dead end unit available in the laboratory. Membrane has been pressurized to 10 bar for an hour to reduce the membrane compaction effect before the test started. The stirring speed was set to 300 rpm. Then, membrane was pressurized with different pressure 2,4,6,8 and 9 bar for water permeability test. Membrane permeability can be obtained from the graph of permeate flux against operating pressure. The permeate flux of the support membrane was obtained by using this equation:

$$J = \frac{v}{A\,t} \tag{1}$$

where J (L/m² h) is permeate flux, V is the permeate volume (L), A is the membrane effective area (m²) and t is the time of testing (h) (Low et al. 2015).

TFC FO MEMBRANE PERFORMANCE EVALUATION

FO system with a Sterlitech CF042 cell measuring 12.7 cm × 10 cm × 8.3 cm was used to evaluate the performance of TFC membrane. The active layer of TFC membrane was set to face the feed solution. 1 L of DI water was used for feed solution while 0.5 L of NaCl (1M) was used for draw solution with the fact that the volume of a solution has no significant effect on the water flux in forward osmosis membranes as been mentioned in previous study by (Law & Mohammad 2017)

Both solution was circulated in a closed loop counter-current by aid of two peristaltic pump (BT600-2J, LongerPump, China). A digital balance was used to record the weight changes in draw solution as illustrated in Figure 1 below:
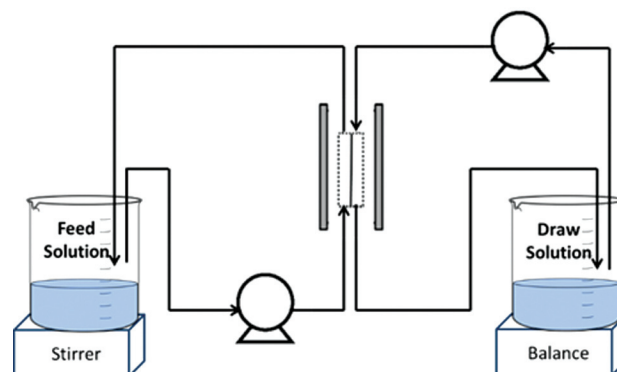

FIGURE 1. Bench scale FO system diagram

Finally, the water permeation flux, J_w can be obtained by this equation:

$$J = \frac{\Delta m}{\rho A \Delta t} \tag{2}$$

where Δm (g) is the weight of permeate water, Δt (h) is the testing duration, ρ is the density of water and A is the effective area of membrane (m²) (Low et al. 2015). The salt leakage usually referred to reverse salt diffusion from the draw solution to the feed solution was determined from conductivity measurements using a calibration curve for the $NaCl_2$ solution. The reverse salt diffusion flux (Js in gm⁻²h⁻¹, abbreviated as gMH) was thereafter determined from the increase of the feed conductivity value using this formula:

$$J_s = \frac{\Delta(c_s v_t)}{\Delta t} \frac{1}{A} \tag{3}$$

where C_s and V_t are the salt concentration and the volume of the feed in the end of FO tests, respectively.

RESULTS AND DISCUSSION

XRD ANALYSIS OF GO

The oxidization of graphite into graphene oxide was confirmed with XRD analysis. The XRD patterns obtained for graphite and synthesized GO are shown in Figure 2. Graphite exhibited a strong peak at 26.575° with interlayer distance of 0.335 nm. Meanwhile, as can be seen in **Error! Reference source not found.**, GO exhibited a peak at 10.787° with interlayer distance of 0.82 nm which showed that graphite was completely oxidized into GO after the chemical oxidation process. Similar findings were observed by other work (Junaidi et al. 2018; Zakaria et al. 2018), where GO exhibited peak at 27.5° while graphite with peak at 10.18°.
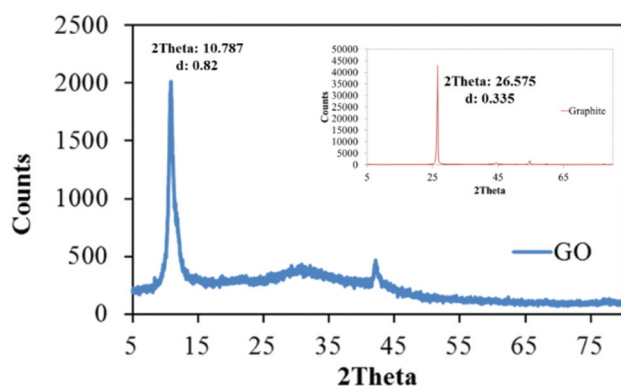
FIGURE 2. The XRD patterns for graphite and GO synthesized

FIGURE 3. FT-IR spectra of graphite and GO synthesized

FTIR ANALYSIS OF GO

Based on the observation of the IR-spectrum of graphite in Figure 3, the O-H stretch can be seen at the peak at 3610 cm^{-1} while the peak at 1677 cm^{-1} was due to the C = C vibration (Ganesh, Isloor & Ismail 2013) changes in FT-IR spectra of graphite was obvious after it was fully oxidized into GO as being shown in Figure. The strong C = O stretch can be seen in GO spectra at 1621 cm^{-1}. Other than that, the peak near 3565 cm^{-1} was due to the O-H stretching vibrations whereas peak at 1224 cm^{-1} and 1417 cm^{-1} were formed from the vibrations of epoxy C-O and C-OH respectively. The FT-IR results showed that the oxygen functional groups were successfully established onto the graphite surface during the oxidation reaction, which produced the desirable GO products. This result was consistent with the findings by other researchers (Haan et al. 2018; Rezaee et al. 2015).
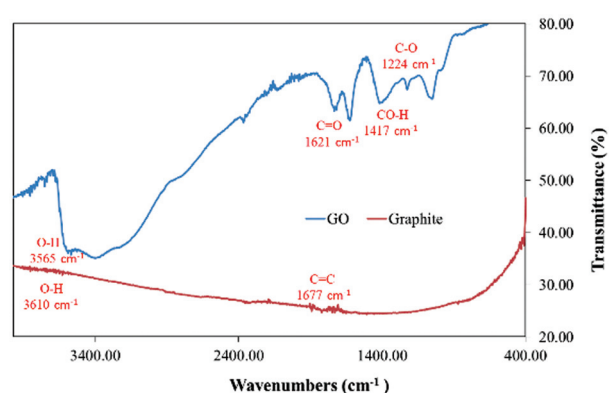
CHARACTERIZATION OF MEMBRANE SUPPORT LAYER

FESEM images in Figure 4 showed the membrane morphology after incorporation of GO nanoparticles. Pure PSf membrane tends to have a few macrovoids with spongy structure at the bottom part of the membrane. On the other hand, after GO has been added at concentration of 0.1, 0.25 and 0.5 wt%, more macrovoids were present and spongy structure was reduced. The morphology of membrane has changed as GO loading was increased, more macrovoids were present and reduce the spongy structure. The incorporation of GO increased the speed of phase inversion process in which such modification causes the formation of microvoid and a spongy structure in the membrane as mentioned by many other works (Chung et al. 2017; Wang et al. 2012). Similar observation has been reported previously by Zinadini et al. (2014), where porosity of nanofiltration (NF) membrane increased with increasing GO content. This was supported by some studies which revealed that the membrane porosity has been increased after incorporation of GO due to the formation of larger finger-like voids (Wang et al. 2015).
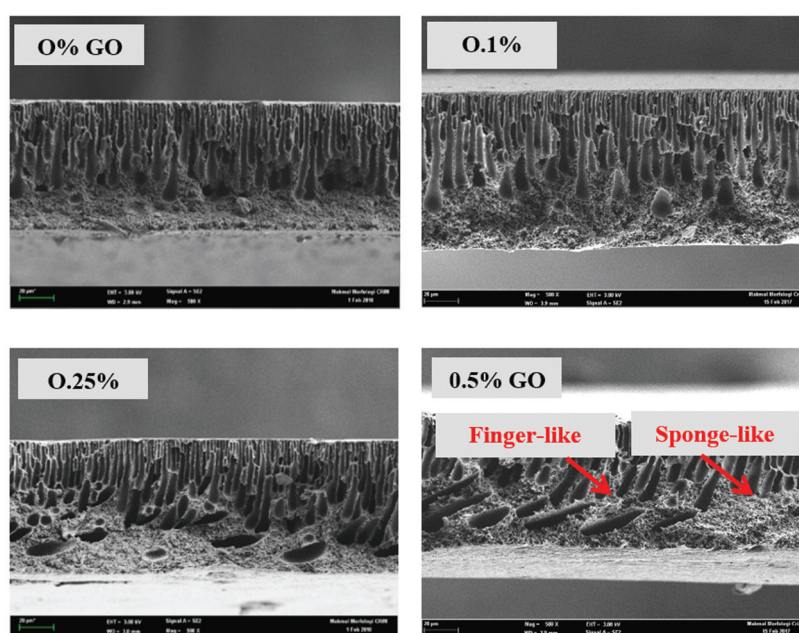

FIGURE 4. Cross-section images of the membranes support

AFM was conducted to evaluate the surface roughness of the fabricated membrane support. Based on Figure 5, it can be seen that the dark areas represented the pores of the membranes. It was revealed that the pure PSf membrane support exhibited average roughness, Ra = 7.034 nm and root mean square of surface roughness, Rms = 8.931 nm. Meanwhile, PSF/GO membrane support exhibited sharper and denser asperities in comparison to the pure PSf membrane. Particularly, as GO loading has been increased to 0.5 wt%, the

roughness values were decreased and increased again at GO loading greater than 0.5 wt%. The presence of GO has proven to reduce the surface roughness of PSf/GO, which can be seen in the roughness value at GO-0.5. This was due to the fact that at low concentration of GO, the low electrostatic interactions among the GO resulted in collocation in membrane leading to smoother surface of the membrane. Hence, it could reduce the membrane roughness and thus creating smooth surface (Qiu et al. 2009).
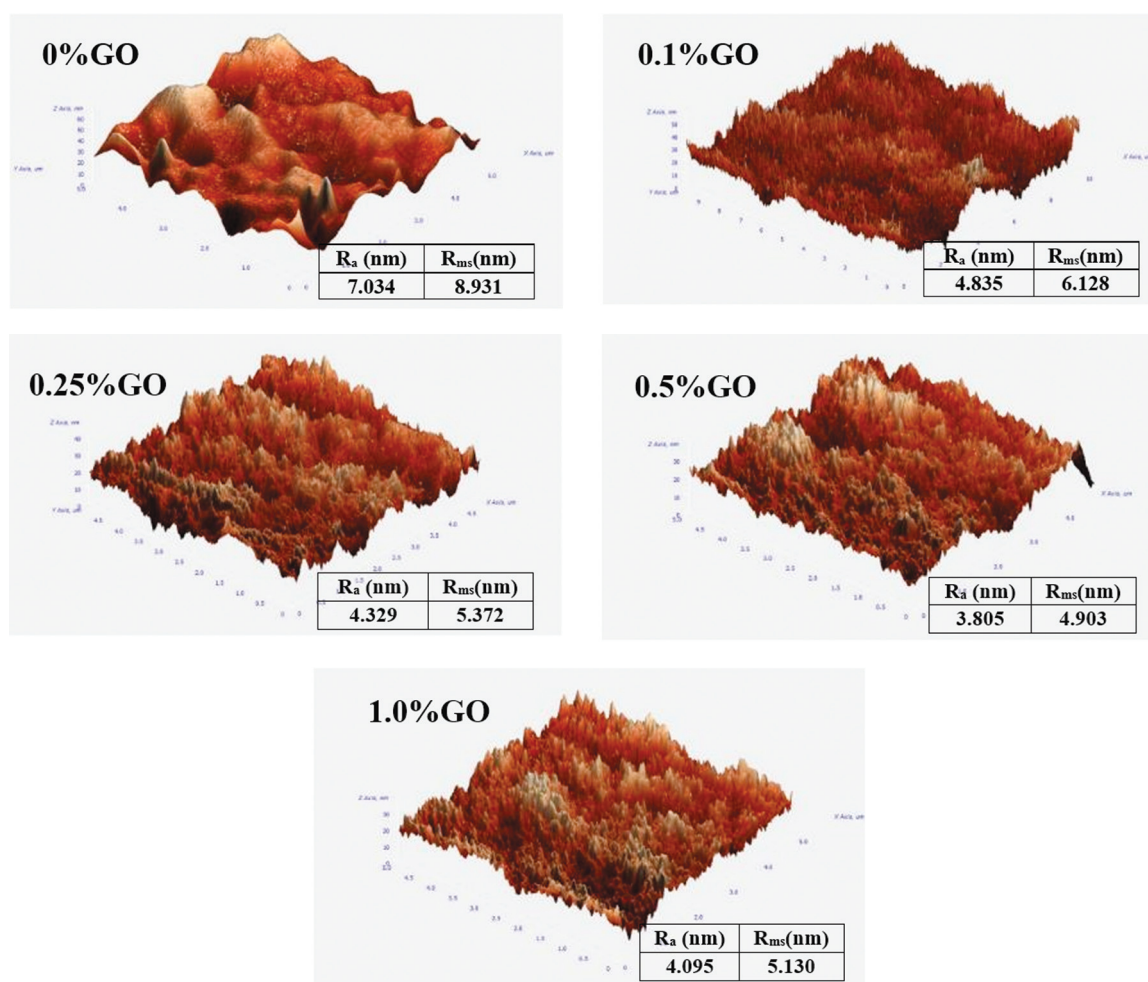

FIGURE 5. The three dimentional surface morphology of the prepared membrane support

The membrane hydrophilicity has been analyzed by contact angle test. As being reported in Figure 6 below, the contact angle of pure PSf membrane was 82° and was significantly reduced to 66° when 0.5 wt% has been added into the membrane support layer. This has been also proven by many previous research works which reported that membranes showed lower contact angle after incorporation of hydrophilic nanomaterials (Y. Wang et al. 2013; Xu et al. 2014; Zinadini et al. 2014). The presence of oxygenous functional groups such as hydroxyl, epoxy groups and carboxyl groups in GO has increase the hydrophilicity of the membrane. This was supported by a study conducted by Zhao et al. (2013) which reported that the addition of graphene to the PVDF membrane

improved the surface hydrophilicity and pure water flux of the membrane On the other hand, the incorporation of GO into the PES membrane has been investigated by Zinadini et al. (2014) in which their membranes showed significant improvement in water flux due to the increasing hydrophilicity of the membrane. However, further increase of GO wt% greater than 0.5 wt% has increased the contact angle value. This phenomena happened as incorporation of higher GO loading resulted in higher viscosity of casting solution which in turned, reduced the membrane pore size and porosity as explained by (Rezaee et al. 2015) in one of their publications. The viscous casting solution may delay the exhange rate between solvent and non-solvent. Some studies reported that
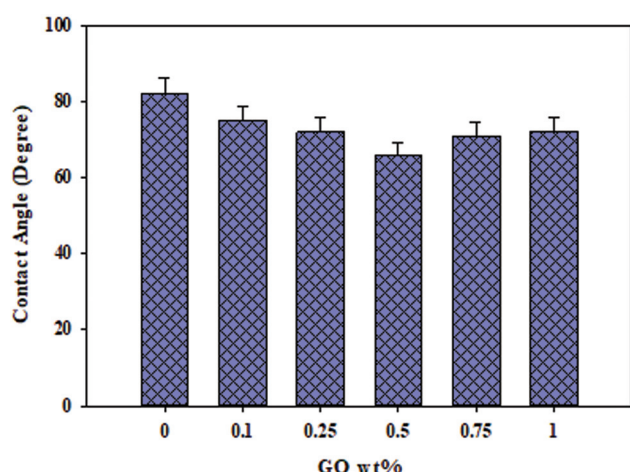
FIGURE 6. Contact angle for different type of membrane based on GO wt%

in this situation, the decrease in hydrophilicity of membrane might be due to the pore blockage by high concentration of GO (Wang et al. 2012).

The water permeability of the membrane support started to increase when GO has been incorporated as comparison to the pure PSf membrane as can be seen in Figure 7. Unfortunately, further increase of GO addition at 0.75 and 1.0 wt% significantly reduce the water permeation through the membrane. This could be due to the irregular placement of GO particles in the membrane (Vatanpour et al. 2011). In addition to this, the water permeation reduction with GO addition more than 0.75 wt% could be due to the pore blockage by high concentration of GO as being observed by other studies (Vatanpour et al. 2011; Wang et al. 2012).
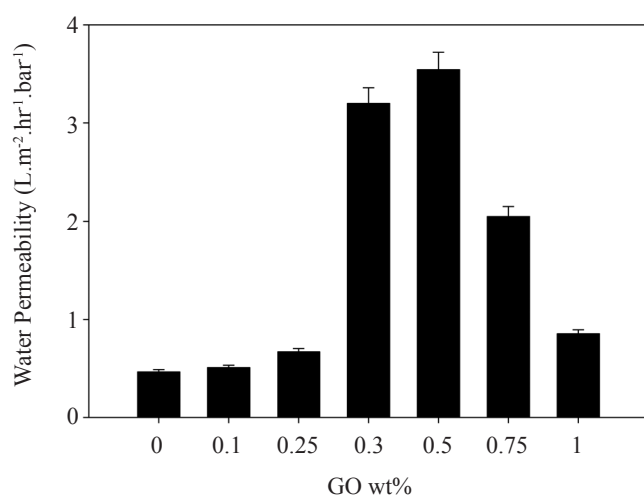

FIGURE 7. Water permeability of membrane support layer

PERFORMANCE EVALUATION OF TFC FO MEMBRANE

TFC FO membrane was fabricated with incorporation of optimal concentration of 0.5 wt% GO and denoted as TFC FO-GO. This concentration was chosen owing to the results from the characterization of membrane support layer as being

reported previously which revealed that at 0.5 wt% of GO, the water permeation and hydrophilicity of membrane has been increased significantly. In this section, the performance of TFC FO-GO has been compared with the pure TFC FO membrane (without GO).

In FO mode, the modified membrane (TFC FO-GO) showed higher water flux, J_w in which it was increased by 44% compared to the pure TFC FO as reported in Table 1 below. In addition to this, reverse salt diffusion was studied as the draw solute leakage through the membrane may affect the osmotic pressure gradient across the membrane. As being reported in Table 1, the TFC FO-GO membrane recorded relatively lower reverse salt diffusion compared to the pure TFC FO membrane. The increase in water flux of TFC FO-GO membrane was due to the physical and chemical properties of GO, which enhance the water permeation through the membrane (Gao, Hu & Mi 2014). Water molecules can physically be transported via the GO nanosheet channels, and chemically GO helps in water molecules adsorption into the membrane due to its hydrophilic functional groups (hydroxyl, carboxyl and epoxy). This is proven by the contact angle result below. The contact angle has been reduced from 68° to 53° after incorporation of GO into the TFC FO membrane which indicates that GO has improved the hydrophilicity of TFC FO membrane.

TABLE 1. Water flux, reverse salt diffusion and contact angle of both TFC membranes

Membrane Type	Water Flux, J_v (L m^{-2}h^{-1})	Reverse Salt Diffusion (g m^{-2} h^{-1})	Contact Angle (°)
TFC FO	2.1	0.03	68.20.1
TFC FO-GO	3.7	0.02	53.30.4

Based on the FESEM images in, the presence of polyamide active layer can be seen by the formation of ridge and valley structures on the membrane surface and via the top cross-section images of TFC FO-GO membrane (Ma et al. 2012). This was supported by the FTIR result in Figure 9. The presence of polyamide layer was confirmed by the existence of bands associated with amide linkages. The carbonyl vibrations exhibited a peak at 1667 cm^{-1} , while the amide II band can be seen at peak 1585 cm^{-1} which is due to the N-H bending and C-N vibrations of the amide group (Belfer, Gilron & Kedem 1999). Amide linkages was formed as can be seen by the peak exhibited at 1667 cm^{-1} due to the reaction of -COOH group from GO with NH$_2$ group from MPD (Saha & Joshi 2009). This result has proven the presence of polyamide layer on the surface of TFC membrane.

CONCLUSIONS

In conclusion, it is believed that the performance of TFC membrane was directly affected by the properties of its support layer. The optimum amount of GO (0.5 wt%) incorporation into membrane support layer has increased
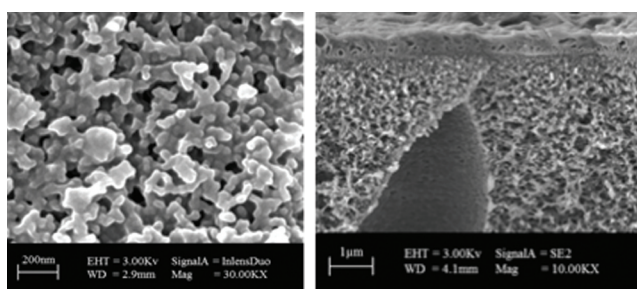
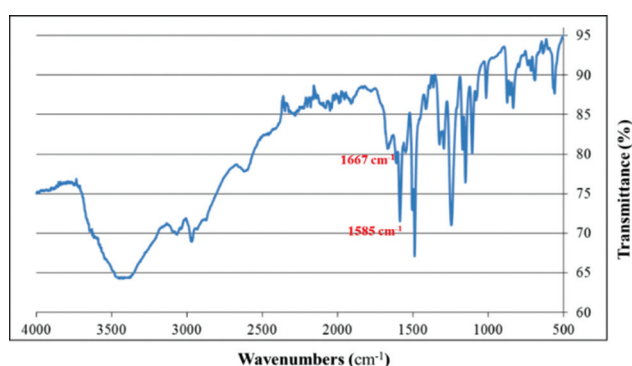FIGURE 8. Surface and cross section FESEM image of TFC FO-GO

FIGURE 9. FTIR result of TFC FO-GO

the water permeation of TFC membrane by 44% compared to the pure TFC membrane. This study has proven that the incorporation of hydrophilic nanoparticle of GO into the membrane support layer can be a good approach in order to develop an effective TFC FO membrane.

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