

## The Effect of Graphene Oxide (GO) Loading for the Enhancement of Nylon 6,6-GO Mixed-matrix Membrane Performance

E. Mahmoudi<sup>a\*</sup>, Y. H. Teow<sup>a,b</sup>, A. W. Mohammad<sup>a</sup>, M. M. Ba-Abbad<sup>d</sup>,  
L. Y. Ng<sup>c</sup> & A. Benamor<sup>d</sup>

<sup>a</sup>Department of Chemical Engineering and Process, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor Darul Ehsan, Malaysia

<sup>b</sup>Research Centre for Sustainable Process Technology (CESPRO), Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor Darul Ehsan, Malaysia

<sup>c</sup>Department of Chemical Engineering, Lee Kong Chian Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, Jalan Sungai Long, Bandar Sungai Long, Cheras, 43000 Kajang, Selangor Darul Ehsan, Malaysia

<sup>d</sup>Gas Processing Centre, Qatar University, P.O. Box 2713, Doha, Qatar

Submitted: 08/06/2020. Revised edition: 27/06/2020. Accepted: 28/06/2020. Available online: 16/07/2020

### ABSTRACT

The fast development of nanotechnology has led to significant improvement in membrane technology for the development of mixed-matrix membranes (MMMs). Graphene oxide (GO) is a new revolutionary addition to the nanomaterial family. The objective of this work is to study the effect of GO loading for the enhancement of nylon 6,6-GO MMMs performance. GO was synthesized from graphite powder and incorporated in membrane matrix through wet phase inversion method. Field Emission Scanning Electron Microscopy, water contact angle, porosity, tensile strength analysis were applied for the characterization of the synthesized nylon-GO MMMs. Whereas, the performance of nylon-GO MMMs was assessed based on its pure water flux and sodium chloride rejection. The incorporation of GO nanoplates into membrane matrix had increased the membrane porosity, surface wettability, and mechanical strength of the synthesized nylon-GO MMMs where the optimum membrane characteristics were obtained by M4 with 3 wt.% of GO nanoplates. Assessment of membrane performance was also supported that M4 has the greatest performance where sodium chloride rejection was increased from 18% for M1 to 53% for M4. The results proved that GO nanoplates are excellent nano-filler material for the synthesis of MMMs. M4 with extraordinary performance has good potential for the application in water and wastewater treatment.

*Keywords:* Mixed-matrix membrane, graphene oxide, nylon 6,6; hydrophilic, sodium chloride rejection

### 1.0 INTRODUCTION

Nylon 6, 6 is a type of polyamide or nylon, made of two monomers containing 6 carbon atoms each. Nylon 6, 6 is an important engineering thermoplastic and greatly used in textile and plastic industries [1] due to

its high mechanical strength, rigidity, and good stability under heat and/or chemicals [2]. Despite its wide application in textile and plastic industries, nylon 6, 6 with its advantages can be used in membrane synthesis.

The fast development of

\* Corresponding to: E. Mahmoudi (email: ebi.dream@gmail.com)

DOI: <https://doi.org/10.11113/amst.v24n2.182>

nanotechnology has led to significant improvement in various applications such as electronics, food, fuel cells, solar cells, batteries, space, fuels, chemical sensors, and fabric. Membrane synthesis with the integration of nanotechnology is also developed in high motion attributed to high attention paid by researchers in this field. Metal and non-metal nanoparticles were embedded into membranes matrix for the formation of mixed-matrix membranes (MMMs) with enhanced performance such as higher water flux, higher permeability, higher rejection, and lower fouling tendency [3, 4]. Among many nanomaterials, graphene and graphene oxide (GO) are considered new revolutionary addition to the nanomaterial family [5]. Attention of the researchers around the world has been drawn toward this wonder nanomaterial by its unique properties, such as 2D carbon nanostructure, high specific surface area, and good thermo-mechanical stability [6].

GO and graphene has been used as nano-filler in nylon family polymer and in the mix matrix material for the enhancement of its thermal and mechanical stability, tensile strength, elongation at break, fracture toughness, and impact failure energy [7]. The objective of this work is to study the effect of GO loading for the enhancement of nylon 6, 6-GO MMMs performance.

## 2.0 METHODS

### 2.1 Materials

Pure fine graphite (particle size < 50  $\mu\text{m}$ ) and formic acid (99 wt.%) were obtained from Merck & Co. Sodium nitrate ( $\text{NaNO}_3$ ), sodium chloride ( $\text{NaCl}$ ) hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), potassium permanganate ( $\text{KMnO}_4$ ) and

sulfuric acid ( $\text{H}_2\text{SO}_4$ ) (98 wt.%) were supplied by Accot Technologies Sdn. Bhd. On the other hand, poly (hexamethylene adipamide) (Nylon-66) was received in pellet form from Sigma-Aldrich.

### 2.2 Synthesis of Graphene Oxide (GO) Nanoplate

GO was synthesized from graphite powder by Hummers method [8]. Typically, 5 g of graphite powder and 2.5 g of  $\text{NaNO}_3$  were mixed into a round bottom flask. 115 mL of  $\text{H}_2\text{SO}_4$  was then added into the mixture under continuous stirring for 30 minutes. Following, the mixture was put in an ice bath to reduce the mixture's temperature below 10  $^\circ\text{C}$ . When the mixture reaches temperature below 10  $^\circ\text{C}$ , 15 g of  $\text{KMnO}_4$  was added gradually into the mixture under continuous stirring and left for reaction at temperature below 10  $^\circ\text{C}$  for 2 hours. Next, the mixture's temperature was increased to 35  $^\circ\text{C}$  and proceed with continuous stirring for 1 hour. The mixture was subsequently diluted with 230 mL deionized water by keeping the mixture's temperature below 100  $^\circ\text{C}$ . Further dilution was conducted by diluting the mixture with 300 mL deionized water. 10 mL of 30%  $\text{H}_2\text{O}_2$  was then added into the mixture to reduce the residual  $\text{KMnO}_4$ . The color of the mixture will gradually change into brilliant yellow, indicating the complete reduction of  $\text{KMnO}_4$ . The mixture was then centrifuged and washed with 5% HCl aqueous solution before freeze dry. Fine brown-coloured GO powder was obtained at the end of the process [9].

### 2.3 Membrane Fabrication

Wet phase inversion method was adopted for the fabrication of nylon-GO MMMs. Membrane polymer

solution was prepared by dispersing the GO nanoplates in formic acid and ultrasonicated for 30 minutes. Nylon 6-6 pellet was then added into homogeneous GO nanoplates suspension. The concentration of GO and the weight ratio of nylon 6-6: formic acid: GO were summarized in Table 1. The mixture was heated to 60 °C with continuous stirring at 300 rpm for 5 hours using silicon oil bath.

Nylon-GO MMM was fabricated by pouring the membrane polymer solution onto a clean glass plate and casted at a thickness of 0.2 mm measured using the casting knife. The glass plate together with casted membrane polymer solution was exposed to air for 15 seconds and immersed into water bath consists of ultrapure water with 10 wt.% formic acid at ambient conditions. The synthesized nylon-GO MMM was then peeled off from the glass plate and rinsed with ultrapure water [10].

#### 2.4 Characterization of GO Nanoplates and Nylon-GO Mixed-matrix Membranes

X-ray diffractometer (XRD), Bruker D8 Advance AXS and transmission electron microscopy (TEM) Philips CM200, model JEOLJEM 2100 were used to identify the crystallinity and surface morphology of GO nanoplates.

Field emission scanning electron microscopy (FESEM), SUPRA 55VP was used to observe the surface morphology and cross-sectional structure of the synthesized nylon-GO MMM. For cross-sectional observation, the synthesized nylon-GO MMM was fracture by immersing in liquid nitrogen. The membrane sample was coated with a thin layer of platinum before FESEM analysis. Water contact angle of the synthesized nylon-GO

MMMs was measured using Kruss GmbH FM12MKE easy drop machine. Whereas, the tensile strength of the synthesized nylon-GO MMMs was analyzed using CT texture analyzer. Membrane porosity ( $\varepsilon$ ) was determined using gravimetric method [11], as defined in the following equation:

$$\varepsilon = \frac{\omega_1 - \omega_2}{A \times l \times d_w} \quad (1)$$

Where  $\omega_1$  is the wet membrane weight (kg) and  $\omega_2$  is the dried membrane weight (kg) A is the effective membrane area (m<sup>2</sup>), l is the membrane thickness (m), and  $d_w$  is the water density (998 kg/m<sup>3</sup>).

#### 2.5 Performance Evaluation of Nylon-GO Mixed-matrix Membranes

A 300 mL dead-end stainless steel stirred cell, Sterlitech™ HP4750 was used to determine permeate flux and NaCl rejection of the synthesized nylon-GO MMMs. The synthesized nylon-GO MMMs with an effective surface area of 14.6 cm<sup>2</sup> was first placed at the bottom of the stirred cell. It was compacted at pressure of 4 bars with ultrapure water for 20 minutes until a steady permeate flux was obtained. Permeate flux of the membrane was calculated using Equation 2:

$$J = \left( \frac{\Delta V}{A \Delta T} \right) \quad (2)$$

Where J is the permeate flux (L/m<sup>2</sup> h),  $\Delta V$  is the permeate cumulative volume (L), A is the effective membrane area (m<sup>2</sup>), and  $\Delta t$  is the filtration time (h).

**Table 1** Nylon-GO MMMs formulations

Membrane	GO concentration (wt.%)	Ratio of Nylon 6,6: formic acid: GO
M1	0	1:4.55:0
M2	1	1:4.55:0.01
M3	2	1:4.55:0.02
M4	3	1:4.55:0.03
M5	4	1:4.55:0.04

On the other hand, NaCl rejection by the synthesized nylon-GO MMMs was calculated using Equation 3.

$$R = 1 - \frac{c_p}{c_f} \quad (3)$$

Where  $C_p$  and  $C_f$  are the concentration of permeate and feed, respectively.

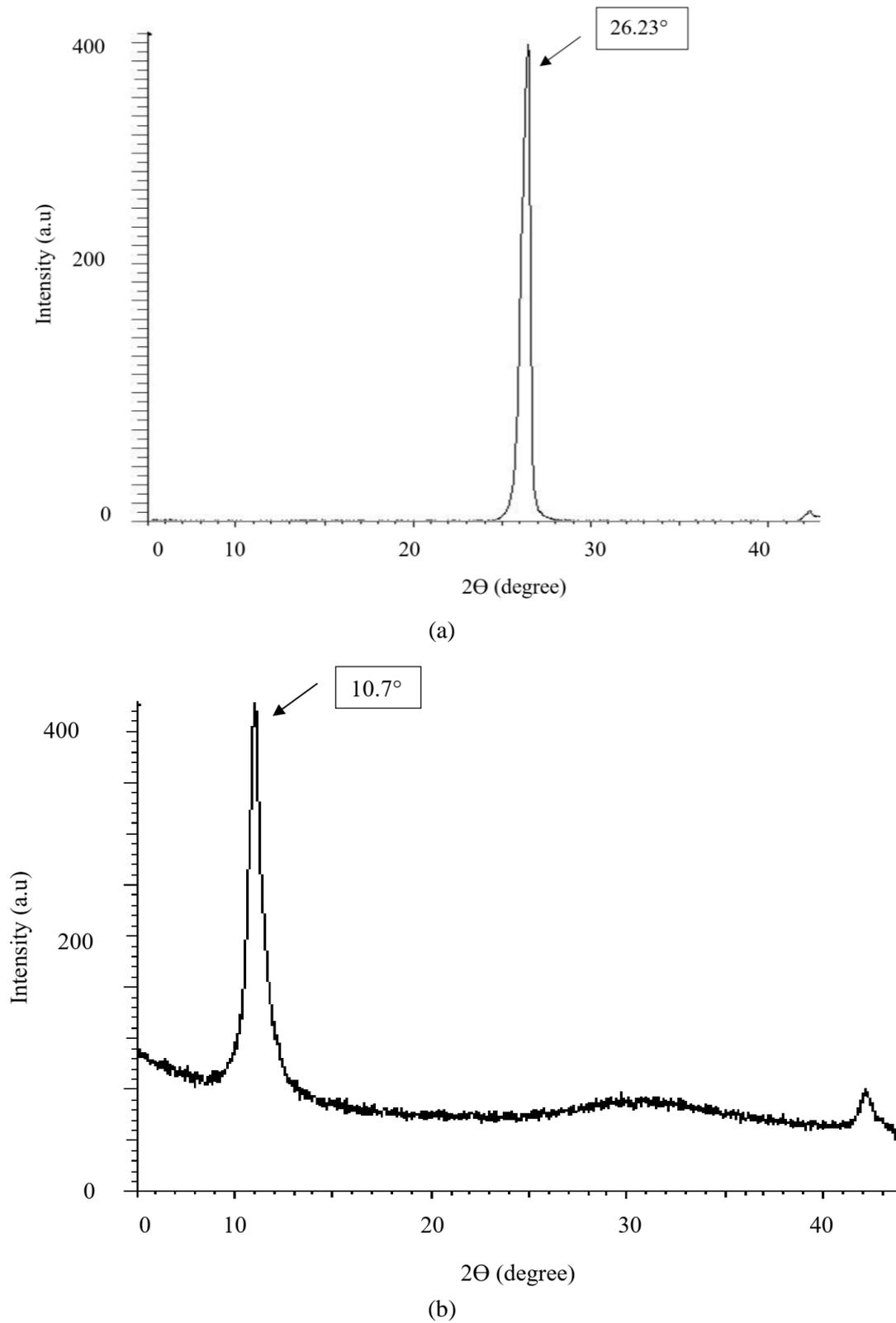
### 3.0 RESULTS AND DISCUSSION

#### 3.1 Characterization of GO Nanoplates

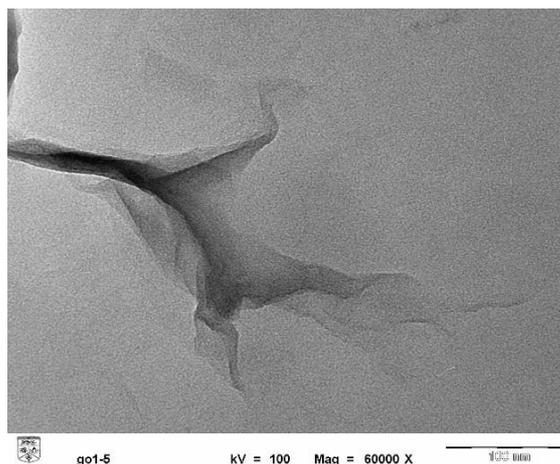
Figure 1 shows the XRD patterns of graphite and GO nanoplates. As shown in Figure 1(a), sharp characteristics peak was appeared at 26.23° for graphite and this characteristics peak

was disappeared after complete oxidation of graphite into GO nanoplates in Figure 1(b). However, a spike at 10.7° corresponding to GO with with a d-spacing of 8.7 Å was existed in Figure 1(b), confirmed the transition of graphite into GO nanoplates [12].

Figure 2 presents the TEM micrograph of the exfoliated GO nanoplates. As depicted in Figure 2, smooth, thin sheet layer of GO nanoplates was formed without any residual graphite deposited on GO surface structure. This supported XRD analysis result on the complete oxidation of graphite into GO nanoplates [13]. Smooth, thin sheet layer of GO nanoplates was a good characteristics for the synthesis of nylon-GO MMMs.



**Figure 1** XRD patterns of (a) graphite and (b) GO nanoplates



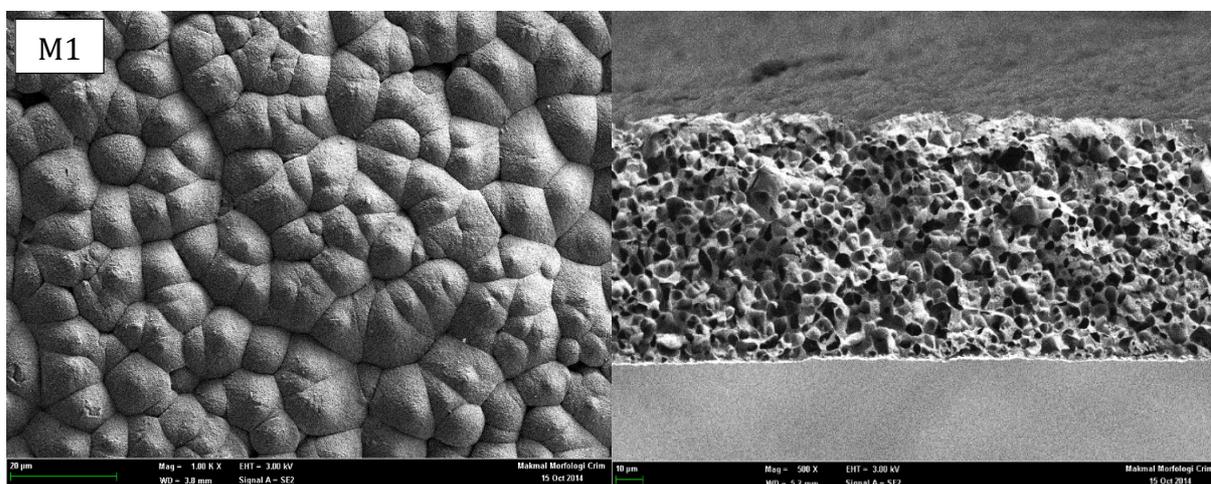
**Figure 2** TEM micrograph of exfoliated GO nanoplates

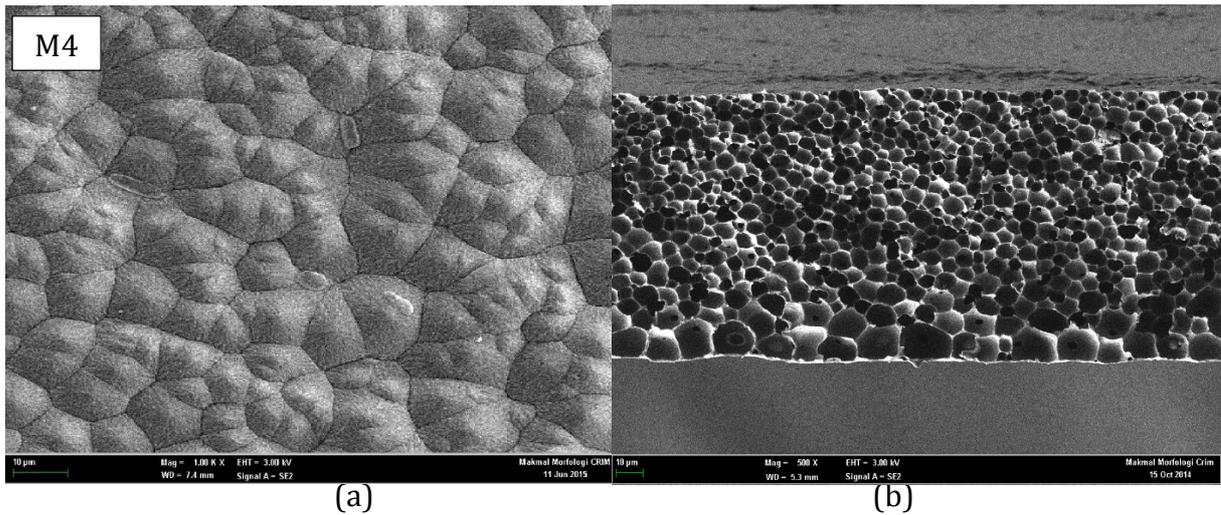
### 3.2 Characterization of Synthesized Nylon-GO Mixed-matrix Membranes

FESEM micrographs of nylon-GO MMMs' surface morphology and cross-sectional structure are depicted in Figure 3. FESEM micrographs of the synthesized nylon-GO MMM indicated in Figure 3 did not present any imperfection or agglomeration of nanomaterial on the membrane surface or in the membrane matrix, suggesting the well distribution of GO nanoplates in membrane matrix [14]. Well distribution of GO nanoplates in membrane matrix would reduce the defect on membrane structure and promote consistency in membrane

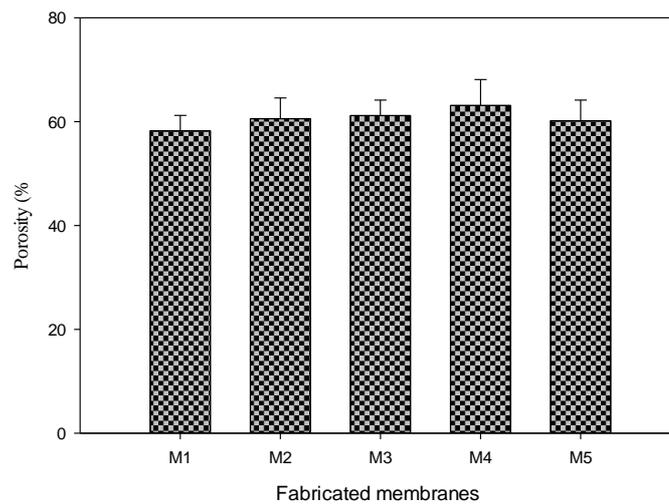
performance [15]. On the other hand, the cross-sectional structure of the synthesized nylon-GO MMM indicated in Figure 3(b) shows that the porosity of M4 was increased dramatically, high porosity of membrane matrix is a favourable characteristic of polymeric membrane for high permeate flux [16].

Figure 4 presents the porosity of the synthesized nylon-GO MMMs. As shown in Figure 4, the membrane porosity was slightly increased with the increasing of GO concentration. The highest membrane porosity was recorded by M4. High porosity of nylon-GO MMMs and the increment of porosity with the increasing of GO concentration was attributed by hydrophilic nature of GO nanoplates [17]. Hydrophilic GO nanoplates led to high exchange rate between solvent and non-solvent in water bath during wet phase inversion process. Rapid exchange rate between solvent and non-solvent contributes to the formation of macro-voids and highly porous membrane structure. However, membrane porosity was decreased as GO concentration was increased to 4 wt.%, probably due to the agglomeration of GO nanoplates in membrane matrix that hindered the membrane pores on membrane surface [18].





**Figure 3** FESEM micrographs of M1 and M4 (a) surface morphology and (b) cross-sectional structure



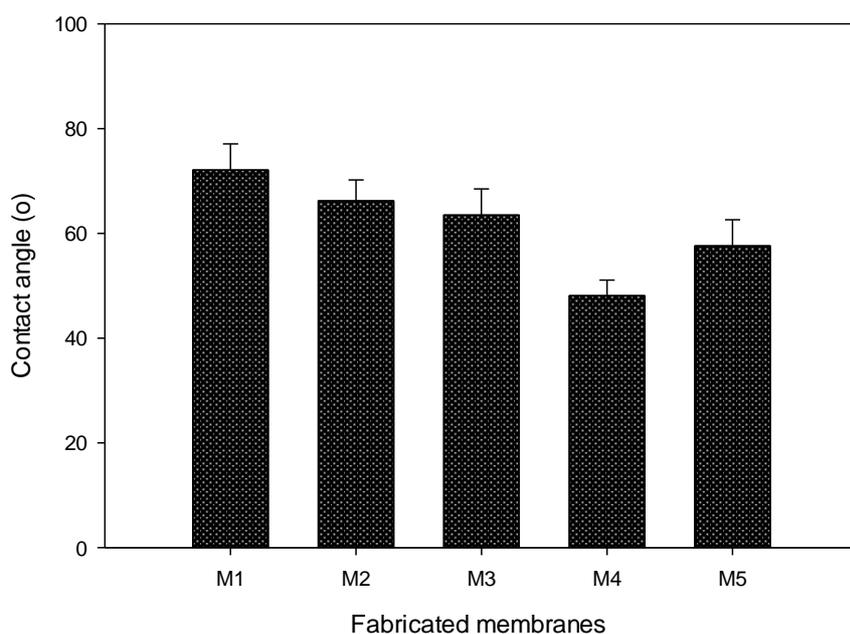
**Figure 4** Porosity of the synthesized nylon-GO MMMs

Surface wettability of the membrane was indicated by the water contact angle value measured on the membrane surface. Generally, lower water contact angle value signifies higher hydrophilic nature of the membrane surface [19]. Figure 5 shows the water contact angle of the synthesized nylon-GO MMMs. The water contact angle value of nylon-GO MMMs was apparently lower than nascent nylon membrane (M1).

Incorporation of GO nanoplates into membrane matrix had increased the membrane hydrophilicity due to the hydrophilic nature of GO nanoplates which can form hydrogen bonding with water molecules [20]. Higher hydrophilicity was a characteristic for nylon-GO MMMs. Most of the foulants in water source are hydrophobic in nature [21]. Hence, hydrophilic membrane surface could reduce the interaction between

membrane surface with hydrophobic foulants, therefore reduce membrane fouling propensity [22]. On top of that, hydrophilic membrane surface was expected in promoting for higher permeate flux. However, M5 shows an increase of water contact angle value after M4. This is probably due to the agglomeration of GO nanoplates in membrane matrix at high GO

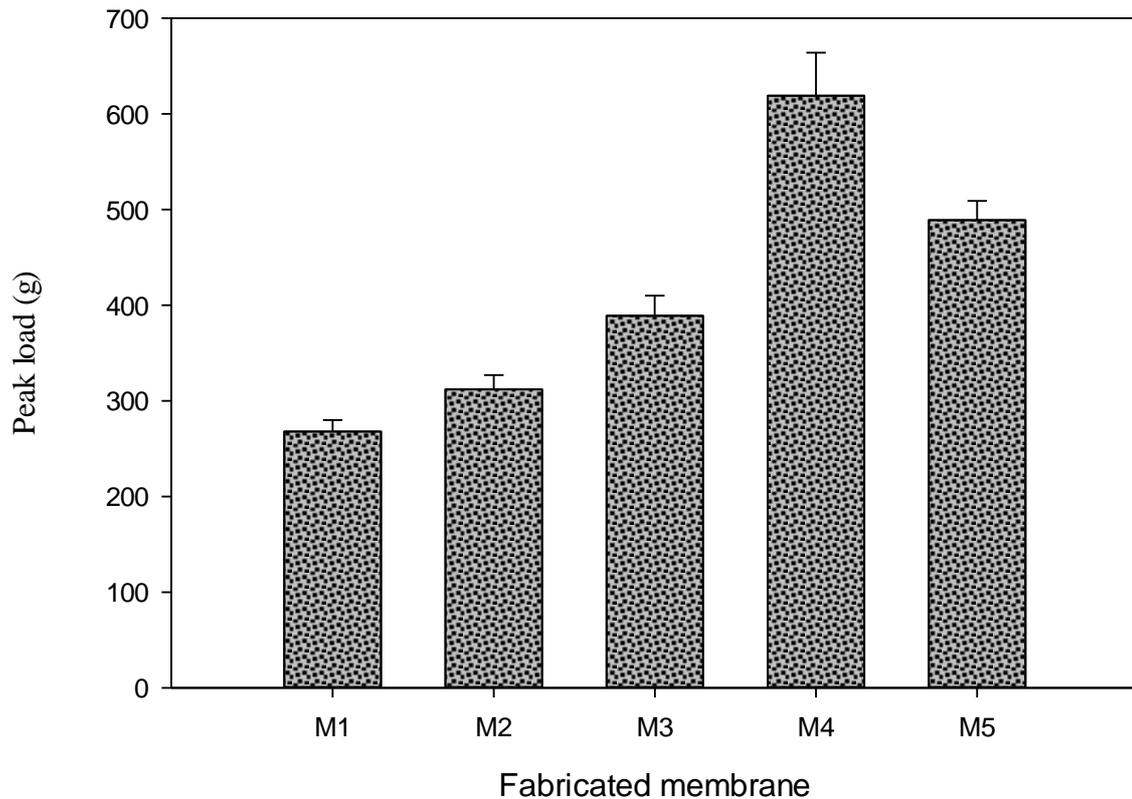
concentration where the effective surface of GO nanoplates was reduced [23]. With this, membrane surface functional groups were also reduced. Similar observation was reported by Zinadini *et al.* (2014) where high blending ratio of GO nanoplates in polymeric membrane formulation has lead to the increasing of water contact angle value [24].



**Figure 5** Water contact angle of the synthesized nylon-GO MMMs

Figure 6 presented the tensile strength of the synthesized nylon-GO MMMs. Mechanical strength enhancement was observed for nylon-GO MMMs with the incorporation of GO nanoplates into membrane matrix. The maximum peak load was recorded

by M4 at 619.5 g with the incorporation of 3 wt.% GO nanoplates into membrane matrix. Similar result was obtained by Jin *et al.* (2013) for a polyamides MMMs incorporated with GO nanoplates [25].

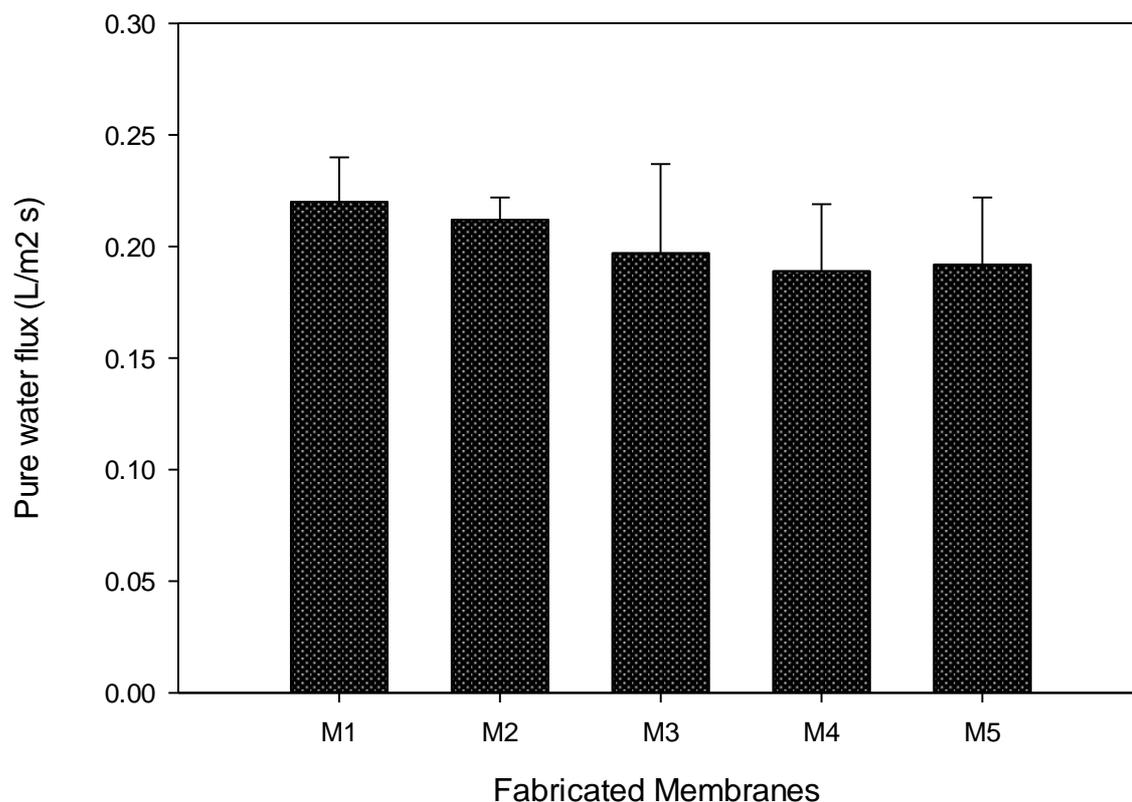


**Figure 6** Tensile strength of the synthesized nylon-GO MMMs

### 3.3 Performance Evaluation of Nylon-GO Mixed-matrix Membranes

Pure water flux of the synthesized nylon-GO MMMs is shown in Figure 7. As presented in Figure 7, there was a slight drop of pure water flux with the increasing of GO concentration. Although membrane surface hydrophilicity and membrane porosity were increased with the increasing of GO concentration and promoting for

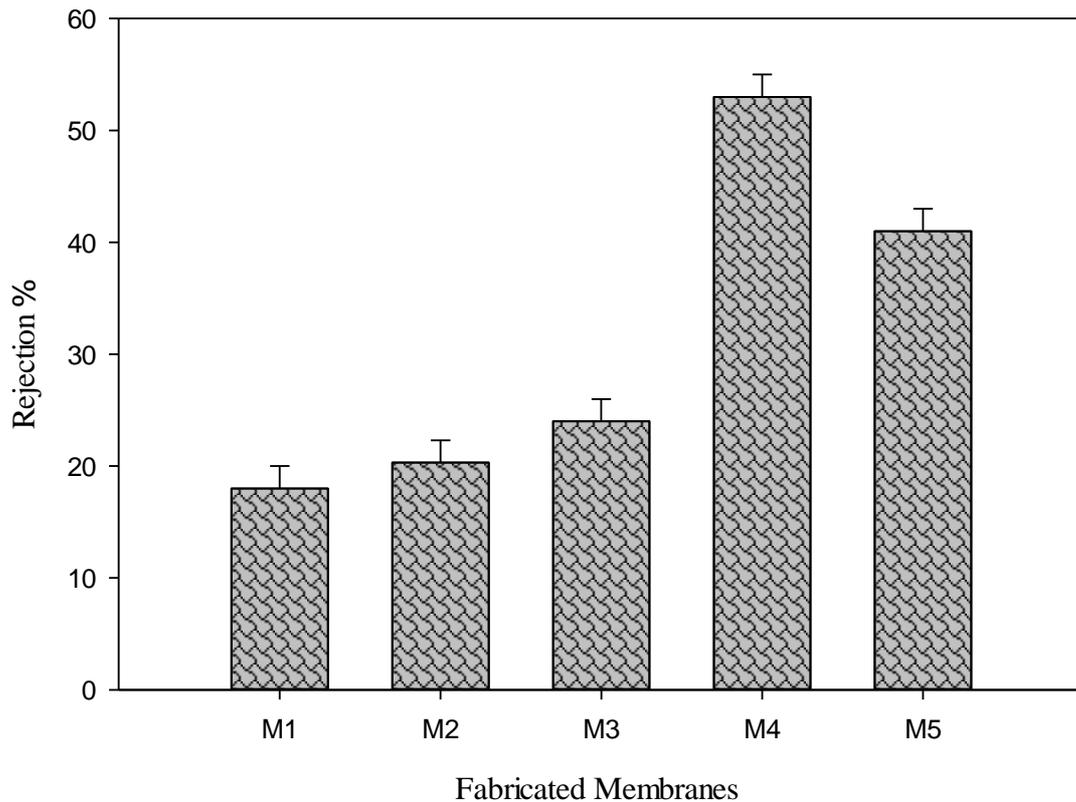
higher pure water flux, the increasing of membrane polymer solution viscosity with the addition of GO nanoplates has formed a denser membrane structure [26]. As membrane morphology is the dominant factor in affecting pure water flux, denser membrane structure at higher GO concentration contributes to slight reduction in pure water flux. However, the pure water flux reduction was not much.



**Figure 7** Pure water flux of the synthesized nylon-GO MMMs

On the other hand, Figure 8 depicted the NaCl rejection of the synthesized nylon-GO MMMs. Comparatively, the results of NaCl rejection has an obvious change than the results of pure water flux for the synthesized nylon-GO MMMs. The rejection was increased from 18% by

M1 to 53% by M4 with the incorporation of 3 wt.% GO nanoplates into membrane matrix. Denser membrane structure with the incorporation of GO nanoplates will reject more NaCl molecules from penetrating through the membrane matrix [27].



**Figure 8** NaCl rejection of the synthesized nylon-GO MMMs

#### 4.0 CONCLUSION

GO nano-plates was synthesized through modified Hummer's method. Smooth, thin sheet layer of GO nanoplates without any residual graphite deposited on GO surface structure was a good characteristics for the synthesis of nylon-GO MMMs. The incorporation of GO nanoplates into membrane matrix had increased the membrane porosity, surface wettability, and mechanical strength of the synthesized nylon-GO MMMs where the optimum membrane characteristics were obtained by M4 with 3 wt.% of GO nanoplates. Assessment of membrane performance on the aspect of pure water flux and NaCl rejection was also supported that M4 was having the greatest performance where NaCl rejection was

increased from 18% for M1 to 53% for M4 without much scarification in pure water flux. The results from this study proved that GO nanoplates are excellent nano-filler material for the synthesis of MMMs.

#### ACKNOWLEDGEMENT

The authors wish to gratefully acknowledge the funding for this work by Long Term Research Grant Scheme (LRGS/2013/UKM-UKM/PT/03) and Dana Modal Insan (MI-2019-017).

#### REFERENCES

- [1] Lin, D.-J., C.-L. Chang, C.-K. Lee, and L.-P. Cheng. 2006. Fine Structure and Crystallinity

- of Porous Nylon 66 Membranes Prepared by Phase Inversion In The Water/Formic Acid/Nylon 66 System. *Eur. Polym. J.* 42: 356-367.
- [2] Ide, F., and A. Hasegawa. 1974. Studies on Polymer Blend of Nylon 6 and Polypropylene or Nylon 6 and Polystyrene Using The Reaction of Polymer. *J. Appl. Polym. Sci.* 18: 963-974.
- [3] Ng, L.Y., A.W. Mohammad, C. P. Leo, and N. Hilal. 2013. Polymeric Membranes Incorporated with Metal/metal Oxide Nanoparticles: A Comprehensive Review. *Desalination.* 308: 15-33.
- [4] Teow, Y. H., B. S. Ooi, and A. L. Ahmad. 2017. Study on PVDF-TiO<sub>2</sub> Mixed-matrix Membrane Behaviour Towards Humic Acid Adsorption. *J. Water Process Eng.* 15: 99-106.
- [5] Geim, A., and K. Novoselov. 2007. The Rise of Graphene. *Nat. Mater.* 6: 183-191.
- [6] Mahmoudi, E., L. Y. Ng, M. M. M. Ba-Abbad, and A. W. Mohammad. 2015. Novel Nanohybrid Polysulfone Membrane Embedded with Silver Nanoparticles on Graphene Oxide Nanoplates. *Chem. Eng. J.* 277: 1-10.
- [7] Xu, Z., and C. Gao. 2010. In Situ Polymerization Approach to Graphene-reinforced Nylon-6 Composites. *Macromolecules.* 43: 6716-6723.
- [8] Hummers, J. R. E. O., and S. William. 1958. Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* 80: 1339-1333.
- [9] Mahmoudi, E., W. L. Ang, C. Y. Ng, L. Y. Ng, A. W. Mohammad, and A. Benamor. 2019. Distinguishing Characteristics and Usability of Graphene Oxide Based on Different Sources of Graphite Feedstock. *J. Colloid Interface Sci.* 542: 429-440.
- [10] Ng, L. Y., A. W. Mohammad, and C. Y. Ng. 2013. A Review on Nanofiltration Membrane Fabrication and Modification Using Polyelectrolytes: Effective Ways to Develop Membrane Selective Barriers and Rejection Capability. *Adv. Colloid Interface Sci.* 197-198: 85-107.
- [11] Vatanpour, V., A. Shockravi, H. Zarrabi, Z. Nikjavan, and A. Javadi. 2015. Fabrication and Characterization of Anti-fouling and Anti-bacterial Ag-loaded Graphene Oxide/Polyethersulfone Mixed Matrix Membrane. *J. Ind. Eng. Chem.* 1-11.
- [12] Xu, C., X. Wu, J. Zhu, and X. Wang. 2008. Synthesis of Amphiphilic Graphite Oxide. *Carbon N. Y.* 46: 386-389.
- [13] Ho, K.C., Y.H. Teow, A.W. Mohammad, W.L. Ang, and P.H. Lee. 2018. Development of Graphene Oxide (GO)/Multi-Walled Carbon Nanotubes (MWCNTs) Nanocomposite Conductive Membranes for Electrically Enhanced Fouling Mitigation. *J. Membr. Sci.* 552: 189-201.
- [14] Teow, Y. H., S. Y. Woo, and A. W. Mohammad. 2018. Studies on the Surface Properties and Fabrication Method of Mixed-Matrix Membrane for Textile Industry Wastewater Treatment. *Desalin. Water Treat.* 135: 303-318.
- [15] Rosnan, N. A., Y. H. Teow, and A. W. Mohammad. 2019. The Effect of ZnO Loading for the Enhancement of PSF/ZnO-GO Mixed-Matrix Membrane Performance. *Sains Malaysiana.* 47: 2035-2045.

- [16] Ho, K.C., Y.H. Teow, and A.W. Mohammad. 2019. Optimization of Nanocomposite Conductive Membrane Formulation and Operating Parameters for Electrically-Enhanced Palm Oil Mill Effluent Filtration using Response Surface Methodology. *Process Saf. Environ.* 126:297-308.
- [17] Sali, S., H.R. Mackey, and A.A. Abdala. 2019. Effect of Graphene Oxide Synthesis Method on Properties and Performance of Polysulfone-Graphene Oxide Mixed Matrix Membranes. *Nanomaterials.* 9: 1-16.
- [18] Chai, P.V., E. Mahmoudi, Y.H. Teow, and A.W. Mohammad. 2015. Preparation of Novel Polysulfone-Fe<sub>3</sub>O<sub>4</sub>/GO Mixed-Matrix Membrane for Humic Acid Rejection. *J. Water Process Eng.* 15: 83-88.
- [19] Teow, Y.H., A.L. Ahmad, J.K. Lim, and B.S. Ooi. 2012. Preparation and Characterization of PVDF/TiO<sub>2</sub> Mixed Matrix Membrane via In Situ Colloidal Precipitation Method. *Desalination.* 295:61-69.
- [20] Ho K.C., Y.H. Teow, W.L. Ang, and A.W. Mohammad. 2017. Novel GO/OMWCNTs Mixed-Matrix Membrane with Enhanced Antifouling Property for Palm Oil Mill Effluent Treatment. *Sep. Purif. Tech.* 177: 337-349.
- [21] Ghani, M.S.H., Y.H. Teow, W.L. Ang, A.W. Mohammad, R. Ngteni, and K.M. Mohamed Yusof. 2018. Fouling Assessment of Tertiary Palm Oil Mill Effluent (POME) Membrane Treatment For Water Reclamation. *Water Reuse Desal.* 8: 412-423.
- [22] Teow, Y.H., A.L. Ahmad, J.K. Lim, and B.S. Ooi. 2013. Studies on the Surface Properties Of Mixed-Matrix Membrane and Its Antifouling Properties For Humic Acid Removal. *J. Appl. Polym. Sci.* 128:3184-3192.
- [23] Ngang, H.P., B.S. Ooi, A.L. Ahmad, and S.O. Lai. 2012. Preparation of Mixed-Matrix Membranes For Micellar Enhanced Ultrafiltration Based on Response Surface Methodology. *Dsalination.* 293:7-20.
- [24] Zinadini, S., A.A. Zinatizadeh, M. Rahimi, V. Vatanpour, and H. Zangeneh. 2014. Preparation of a Novel Antifouling Mixed Matrix PES Membrane By Embedding Graphene Oxide Nanoplates. *J. Membr. Sci.* 453:292–301.
- [25] Jin, J., R. Rafiq, Y.Q. Gill, and M. Song. 2013. Preparation and Characterization of High Performance of Graphene/Nylon Nanocomposites. *Eur. Polym. J.* 49:2617–2626.
- [26] Wu, H., B. Tang, and P. Wu. 2010. Novel Ultrafiltration Membranes Prepared From A Multi-Walled Carbon Nanotubes/Polymer Composite. *J. Memb. Sci.* 362:374–383.
- [27] Linggawati, A., A.W. Mohammad, and Z. Ghazali. 2009. Effect of Electron Beam Irradiation on Morphology and Sieving Characteristics of Nylon-66 Membranes. *Eur. Polym. J.* 45: 2797–2804.