Progress in Engineering Application and Technology Vol. 4 No. 2 (2023) 518–530

PEAT

Journal homepage: http://penerbit.uthm.edu.my/periodicals/index.php/peat
e-ISSN : 2773-5303

Analysis of PVDF/ PES Blended Membrane Incorporated with Graphene Oxide (GO) for Oily Water Treatment

Nurul Ain Mohamed[1], Nurasyikin Misdan[1,*]

[1]Department of Mechanical Engineering Technology, Faculty of Engineering Technology, Universiti Tun Hussein Onn Malaysia, 86400 Pagoh, Muar, Johor, MALAYSIA

*Corresponding Author Designation

DOI: https://doi.org/10.30880/peat.2023.04.02.052
Received 15 January 2023; Accepted 11 February 2023; Available online 11 February 2023

Abstract: Oily wastewater treatment has become necessary due to stringent effluent discharge regulations and the constant desire to reuse treated water. Factors such as wastewater composition (high, medium, or low strength), regulatory constraints, prices, treatment efficiency, and wastewater end use all influence the approach chosen for treating oily wastewater. The microporous polymeric-based membrane has become increasingly used in a wide range of water treatment processes over the years due to significant improvements in its intrinsic properties, particularly hydrophilicity and anti-fouling resistance, as well as low energy requirements and ease of operation. In general, ultrafiltration (UF) membranes with pore sizes ranging from 0.05 to 0.5 m are thought to be adequate for treating oil-water emulsions and producing high-quality permeate; however, their low resistance to oil deposition and adsorption is likely to shorten the membrane's lifespan, particularly when dealing with high concentrations of oily wastewater. The purpose of this study was to look into the potential of a polyvinylidene fluoride (PVDF) / polyethersulfone (PES) blended membrane infused with graphene oxide (GO). PVDF was chosen as the primary polymer because of its anti-oxidation properties, high thermal stability, good organic selectivity, and excellent chemical and mechanical resistance. PES was chosen because it was mechanically and hydrolytically stable, as well as heat and chemically resistant. The presence of GO not only improved the membrane's hydrophilicity and water flux, but it also helped to reduce potential fouling problems. The primary research goals were to fabricate a PVDF/PES composite with GO using the NIPs method, characterise the chemical and physical properties, and analyse the potential performance in oil rejection. PVDF concentrations are 9 wt%, 12 wt%, and 6 wt%, respectively, while GO concentrations are 0 wt% and 0.1 wt%. There are three different PVDF to PES solution ratios: 1:1, 2:1, and 1:2. Contact angle (CA) and Fourier Transform Infrared (FTIR) will be used to characterise the chemical properties of the prepared composite membrane (FTIR). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) will be used to characterise physical properties (AFM). The b(ii) membrane performed the best in this study, with a PVDF to PES concentration of 12 wt% to 6 wt%. This contributed to the 2472.03 L/m2h and has a rejection rate of

Corresponding author: nurasyikin@uthm.edu.my

97.90%. In the future, industries should allow researchers to test their treatment plants using industrial oily wastewater rather than laboratory oily wastewater.

Keywords: Ultrafiltration, Polyvinylidene Fluoride (PVDF), Polyethersulfone (PES), Graphene Oxide (GO), Oily Wastewater

1. Introduction

Oily wastewater is defined as wastewater containing fats, oils, and greases in high concentrations, as well as a variety of dissolved compounds (organic and/or inorganic). It is regarded as one of the most hazardous wastewaters, posing serious environmental and health risks to ecosystems, flora, and fauna [1]. The global increase in oily wastewater discharge, combined with stringent effluent discharge laws and an unwavering desire to reuse treated wastewater, necessitates wastewater treatment.

Treatment of oily wastewater has become necessary due to stringent effluent discharge rules and the constant desire to reuse treated water [2]. The selection of approaches for treating oily wastewater is influenced by factors such as wastewater composition (high, medium, or low strength), regulatory constraints, prices, treatment efficiency, and wastewater end use. Traditional methods for treating oily wastewater include flotation, chemical coagulation, gravity separation, and sedimentation [3]. However, due to operational challenges, high operating costs, the discharge of secondary pollutants, and limited treatment efficacy, these procedures are insufficient [4].

Mixed matrix membrane is frequently used in the treatment of oily wastewater. Given the widespread usage of mixed-matrix membranes (MMMs) for various separation processes as well as biomedical applications, technology for the production of mixed-matrix membranes has attracted a lot of research attention. MMMs are now preferred for research because of their wide variety of features, which include selectivity, strong permeability of desired liquid or gas, antifouling behaviour, and acceptable mechanical strength. However, these properties of MMMs are due to their designed structure, which is possible due to a fabrication process with controlled fabrication parameters and a choice of appropriate materials, such as a polymer matrix with dispersed nanoparticulate based on a typical application [5].

Graphene oxide is made up of a single layer graphene sheet that is covalently bonded to oxygen functional groups on the sheet's basal planes and edges. There are hydroxyl and epoxy groups on the basal planes, and carboxyl, carbonyl, phenol, lactone, and quinone groups can be found on the edges. The polar functional groups on GO make it highly hydrophilic and water-soluble, which is important for processing and chemical derivatization. Furthermore, GO is said to have high mechanical strength/flexibility, a high solute rejection rate, chemical and thermal stability, an excellent hydrophilic surface, and self-stacking properties in the form of laminates, making it suitable for membrane fabrication for water purification applications. [6].

The purpose of this study was to look into the potential of a polyvinylidene fluoride (PVDF) / polyethersulfone (PES) blended membrane infused with graphene oxide (GO). PVDF was chosen as the primary polymer because of its anti-oxidation properties, high thermal stability, good organic selectivity, and excellent chemical and mechanical resistance. PES was chosen because it was mechanically and hydrolytically stable, as well as heat and chemically resistant. The presence of GO not only improved the membrane's hydrophilicity and water flux, but it also helped to reduce potential fouling problems. The primary research goals were to fabricate a PVDF membrane infused with GO using the NIPs method, characterise the chemical and physical properties, and assess the potential performance in oil rejection. PVDF concentrations are 9 wt%, 12 wt%, and 6 wt%, respectively, while GP concentrations are 0 wt% and 0.1 wt%. There are three different PVDF to PES solution ratios: 1:1, 2:1, and 1:2. Contact angle (CA) and Fourier Transform Infrared (FTIR) will be used to characterise

the chemical properties of the prepared composite membrane (FTIR). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) will be used to characterise physical properties (AFM).

2. Materials and Methods

2.1 Material and chemical

The main material for this polymer membrane were the Polyvinylidene fluoride (PVDF) and polyethersulfone (PES). PVDF was one of the hydrophobic material while PES was the hydrophilic material. This combination of materials was composed to produce a high-water flux and can withstand with the harsh situation in filtration process. The concentration of this polymer was set to be 18wt%/.While graphene oxide, functioned in enhancing the performance of the membrane. Polyvinlyppyrrolidone (PVP) was used to allow more water pass through the membrane since it contained hydrophilic character. Both GO and PVP were supplied from Sigma Aldrich. The methyl-2-pyrrolidinone (NMP) with purity 99% was used as a solvent from Merck Sdn Bhd:

2.2 Dope solution preparation

PVDF/ PES composite membranes will be prepared by mixing 18 wt% PVDF/ PES composite solution with different ratio which are 1:1, 2:1 and 1:2 with NMP, and then it will be added with GO with concentration of 0.1 wt% and 0 wt%. The additive was added gradually to the solution to avoid precipitation. The two solutions will be stirred separately for 24 hours until a uniform solution is obtained. It is then sonicated for 4 hours to eliminate bubbles that will formed during the stirring process. Table 1 shown the preparation of the dope selection

The 60g of NMP solution was weighted using digital scale. The NMP solution was then transferred to the Duran bottle. 1g of PVP and 9g of PVDF was weighted and then transferred to the same Duran bottle. Magnetic-bar-stir was put into the Duran bottle as the stirrer. The hot plate was switched on and was adjusted according to the recommended temperature; above 50°C and speed; 5 and was left for 24 hours. After 24 hours, 9g of PES was put into the Duran bottle with the remaining NMP solution and was left until all the material were fully dissolved and the temperature was set to only 30°C. After 24 hours, 9g of PES was put into the Duran bottle with the remaining NMP solution ad was left until all the material were fully dissolved and the temperature was set to only 30°C. Finally, if the membrane has GO loading, then 0.1g of GO is transfer to the Duran bottle and was placed onto the hot plate but the temperature knob is switch off.

Table 1: Dope selection

Membrane	Ratio	PVDF (wt%)	PES (wt%)	PVP (wt%)	GO (wt%)	NMP (wt%)	Total (wt%)
a(i)	1:1	9	9	1	0	81	100
a(ii)	1:1	9	9	1	0.1	80.9	100
b(i)	2:1	12	6	1	0	81	100
b(ii)	2:1	12	6	1	0.1	80.9	100
c(i)	1:2	6	12	1	0	81	100
c(ii)	1:2	6	12	1	0.1	80.9	100

2.3 Flat sheet membrane preparation

After all the material was completely dissolved, the casting process was continued. The dope solution was poured onto a clean glass plate and was using a glass rod. Then, the membrane was pulled from the glass and immersed again in another basin of clean water and was left for 24 hour .The next day, the membrane was hanged in to let it naturally dried.

2.4 Membrane testing performance

2.4.1 Permeate flux

The Sterlitech Cross/Tangential Flow Cells was used. The model used has max pressure of 20 bar and max flow rate of 1 LPM. For every 10ml of volume filtrates, the time were collected and recorded for each one of the membranes. Firstly, the feed solution was set by 1000ml of the pure water and membrane were changed after all the data were collected. Then the feed solution was changed with oily wastewater. The oily wastewater was prepared by adding 3g of cooking oil into 1000ml of pure water. Then the process was repeated for those 6 membranes. The flux was calculated using formula:

$$J_w = \frac{V(L)}{A(m^2)x\ t\ (h)} \quad Eq.1$$

Where V was the volume of filtrates, A is area of active membrane and t was time required by the membrane to filter the solution.

The oily wastewater was made by mixing the 1000ml of Reverse Osmosis water with the cooking oil with concentration of 3g per litre that equal to 3000 ppm.

2.4.2 Oil rejection

Firstly, all the membranes were tested using the crossflow machine. The feed solution is the oily wastewater with 3000 ppm. The filtrates that pass through were collected and was placed into cuvette and labelled according the membrane that've tested. The filtrates were tested using GENESYS 10S UV-Vis that displayed the concentration of the solution tested. The crucial part was feed solution must be tested first. Because it will be indicated that the rejection was really working or not. Theoretically, the filtrate concentration must be lower than the feed solution. From the results, the oil rejection was calculated using formula:

$$R(\%) = \left(1 - \frac{C_p(ppm)}{C_f\ (ppm)}\right)x100\% \quad Eq.2$$

Where C_p was the permeate concentration while C_f was the feed concentration

2.5 Membrane characterization

2.5.1 Characterization by Scanning Electron Microscope (SEM)

Scanning electron microscope (SEM) was used to know the morphological such as the feature of the membrane surface and the model used was Hitachi SU1510 SEM. The sample of membranes were coated with titanium in order to let the electron pass through them. So that it can produced magnified and clear image.

2.5.2 Characterization by Atomic force microscope (AFM)

Atomic force microscope (AFM) was used to evaluate the topographic like surface roughness and the model used was XE-100. Like usual, all the membrane was cut into the smaller size like 1.5cm x 1.5cm and were attached to a clear glass.

2.5.3 Characterization by Fourier Transform Infrared (FTIR)

FTIR was utilised to create an infrared absorption spectrum in order to study the chemical bonds in the membrane, and the model used was Perkin Elmer Spectrum 100. FT-IR spectrometer. The sample of membrane was cut at least covered the testing area and the result were displayed in the graph form.

2.5.4 Characterization by Contact angle

Contact angle was used in determining the hydrophobicity or hydrophilicity of the membrane. The sample of membrane was cut. VCA Optima-AST model was used to get the contact angle of the sample of membrane. The result of contact angle was given in the image file and if the angle is less than 90˚ it indicated it was the hydrophilic material and if the angle was more 90˚ it revealed it was the hydrophobic material.

3. Results and Discussion

3.1 Analysis on membrane surface

Figure 1 shows the SEM images of membrane's surface for the 6 membranes. The surface pores of a(i) membrane was clearer and shows the most evenly distributed Thus its images can be observed easily with the 1200 magnification. The less pore width in membrane might be explained by the delayed exchange rate of solvent of NMP and non-solvent (water from the coagulation bath) during the phase of Non-solvent Induced Phase Separation Process (NIPS), which was caused by the increased viscosity of the dope solution utilised.

3.2 Analysis on surface roughness

Figure 2 shows the surface roughness of all the membranes tested. It shown the membrane that has higher concentration of PES (membrane c) contribute to the rougher mean surface that has been indicated by the lowest roughness value[7] The surface roughness of the membrane's changes when the PES or PVDF ratio increases. This is due to rising polymer concentration, which leads membranes to become more compact and thicker, resulting in rougher surface membranes. Meanwhile, the comparison between the membrane without GO and the membrane with it. According to the observations, the presence of GO causes a higher roughness of the surface membrane. This could be due to the quick exchange of solvent and non-solvent during the phase inverse process, which affects the membrane's porosity.

3.3 Analysis on surface hydrophobicity

Figure 3, illustrated the contact angle of those six membrane and the trend of these contact angle value was the membranes that has been added with GO, have the higher value of contact angle. For example, membrane b(ii) has higher contact angle value that was 74.70˚ compared to b(i) that only has 68.70˚ and c(ii) membrane that has 61.60° compared to c(i) with 55.40˚. The contact angle of the membranes should become hydrophobic which mean it should larger and nearer to 90°[8], with the presence of PVDF, since it shows the crystalline nature. However, several conditions have resulted in membrane flaws. Especially, the higher concentration of hydrophilic material which are PES and GO compared to the concentration of hydrophobic one; PVDF. Because of the oxygen-containing functional groups on its hydrophilic surface, the addition of the GO, which has a high hydrophilic nature, promotes a higher potential to adsorb and store water molecules.

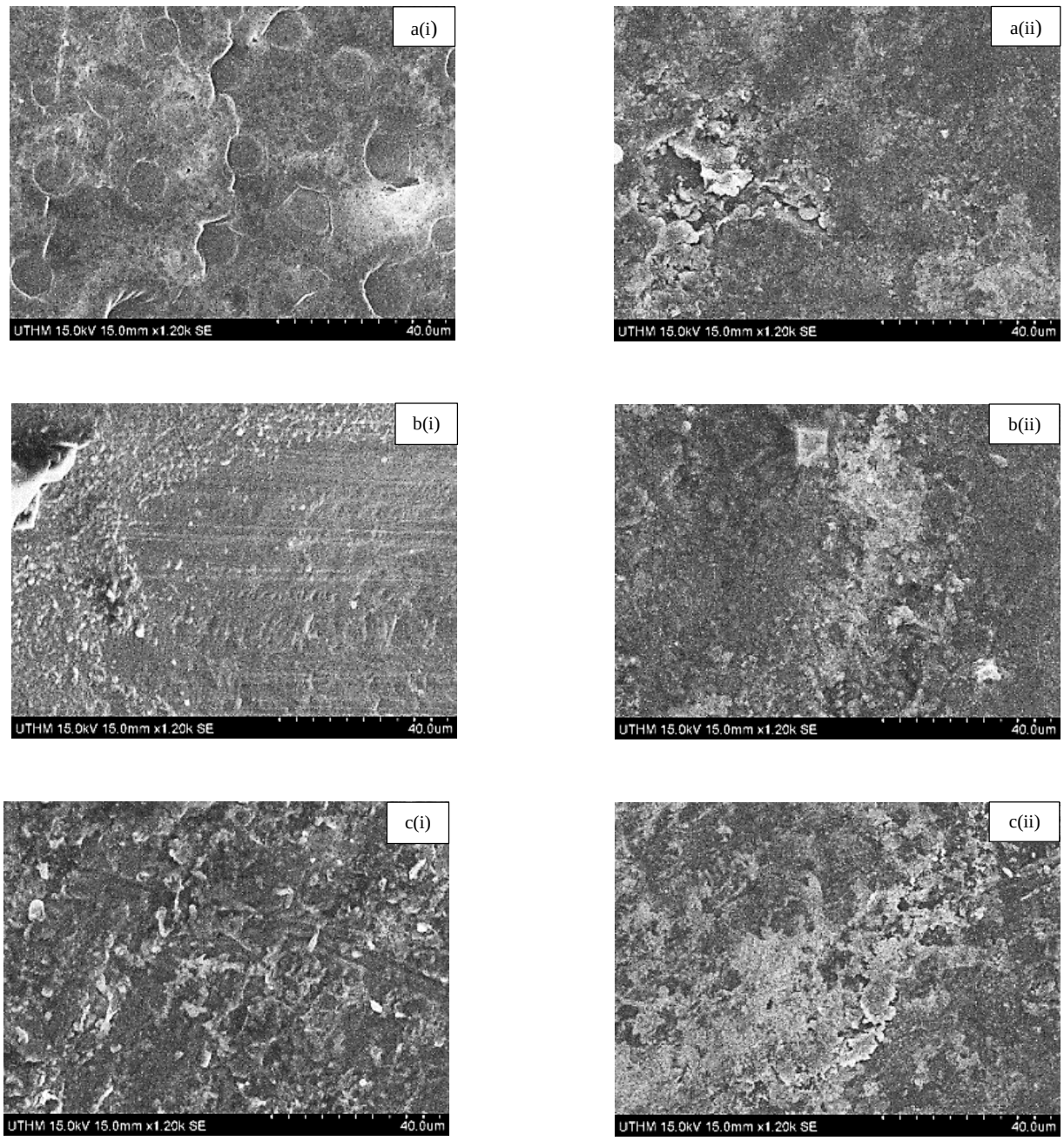
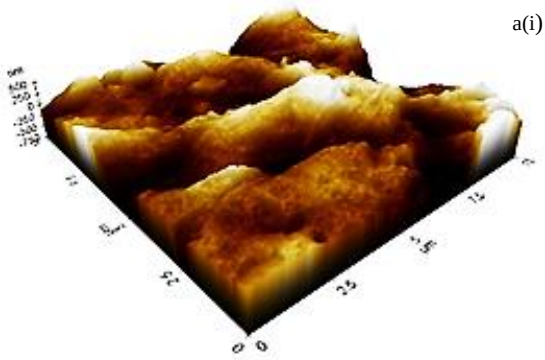


Figure 1: SEM images of membrane surface

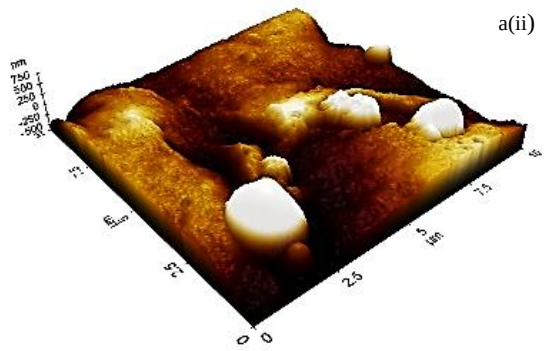
R_a=134.233 nm

a(i)



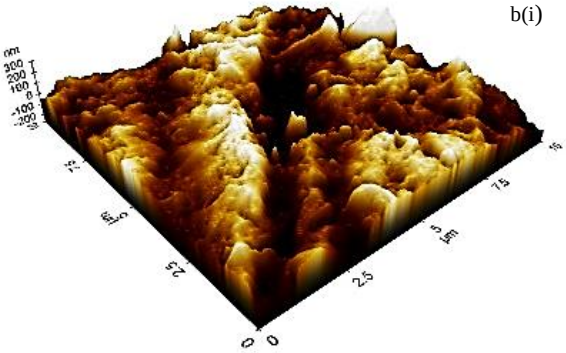
R_a=127.353nm

a(ii)



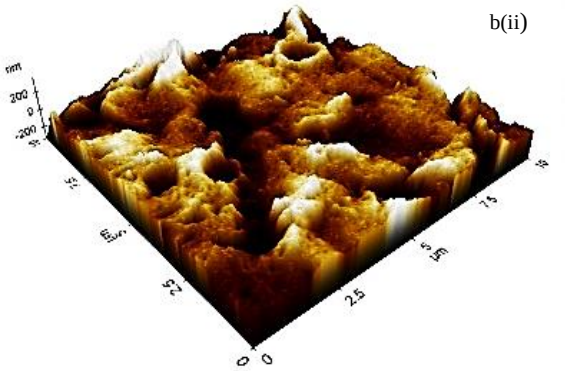
R_a=55.529 nm

b(i)



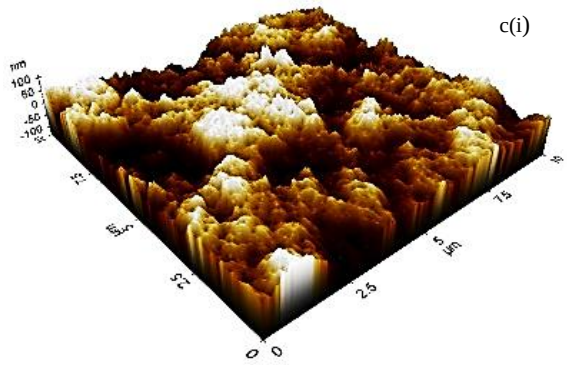
R_a=56.725 nm

b(ii)



R_a=23.976 nm

c(i)



R_a=21.288 nm

c(ii)

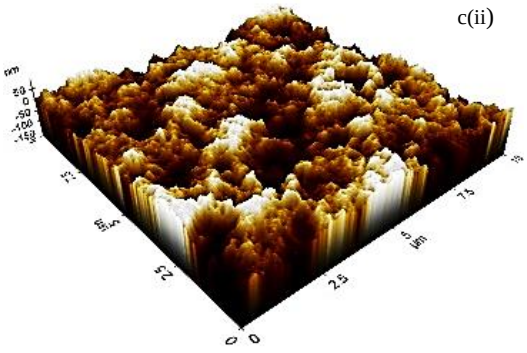


Figure 2: AFM images of membrane surface

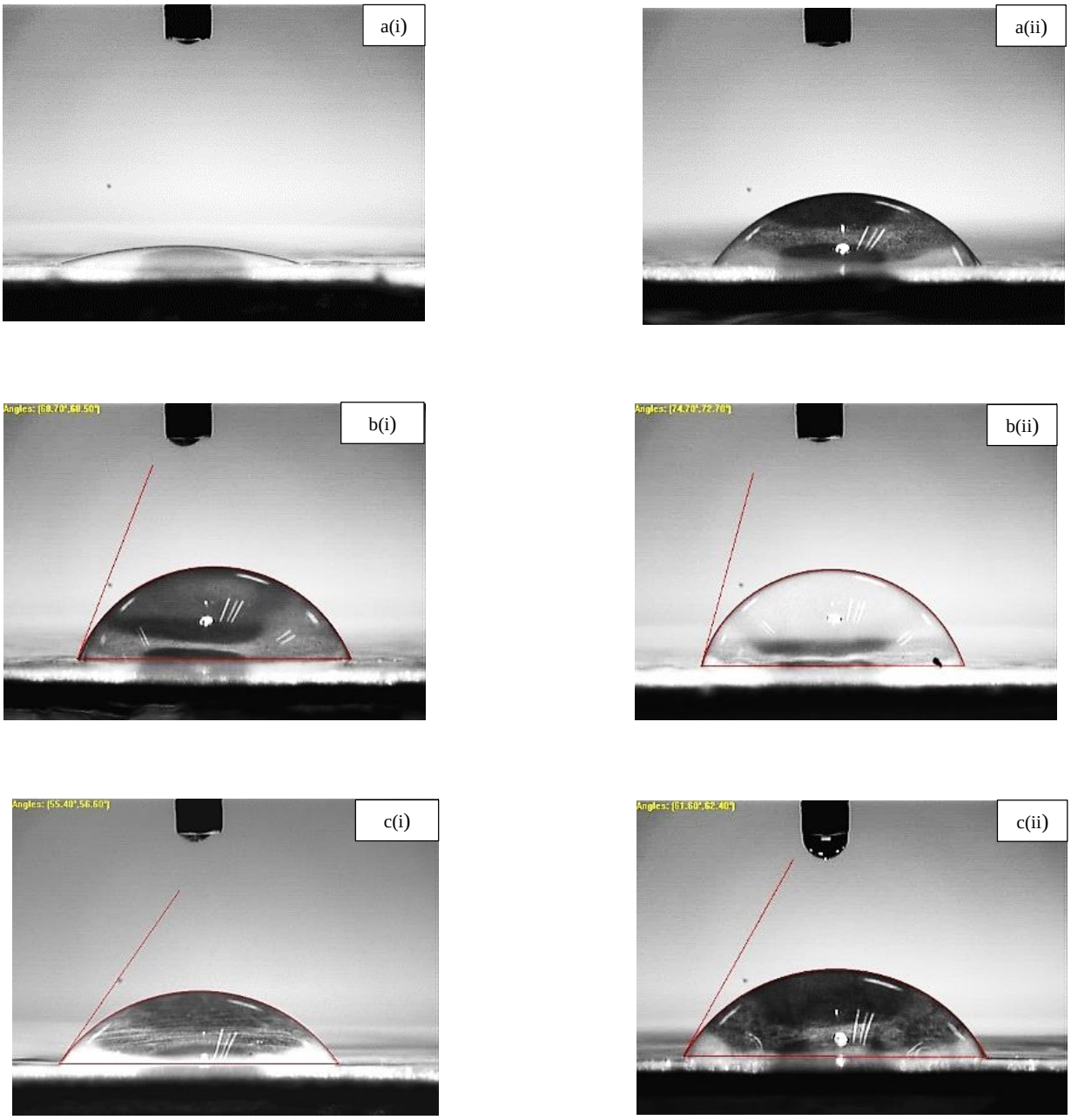


Figure 3: Contact Angle of the membrane

3.4 Analysis on chemical bonding of the membrane

The FTIR spectra of PVDF/PES blended membrane were indicated in Figure 4 and 5. The bands at 948 cm^{-1} was associated to the characteristic of PVDF. The blended particle of PES resulted in the sharp peak around 1578 cm^{-1} Then, the absorption band at the peak at 1721.88 cm^{-1} indicates stretching of C=O due to the occurrence of the NMP.[9] Next the peak that shown the presence of GO which is 3429 cm^{-1} was not obviously appeared at figure 5. This since the concentration of GO was very low to show clearly its behaviour. Thus, it cannot be captured by this FTIR.

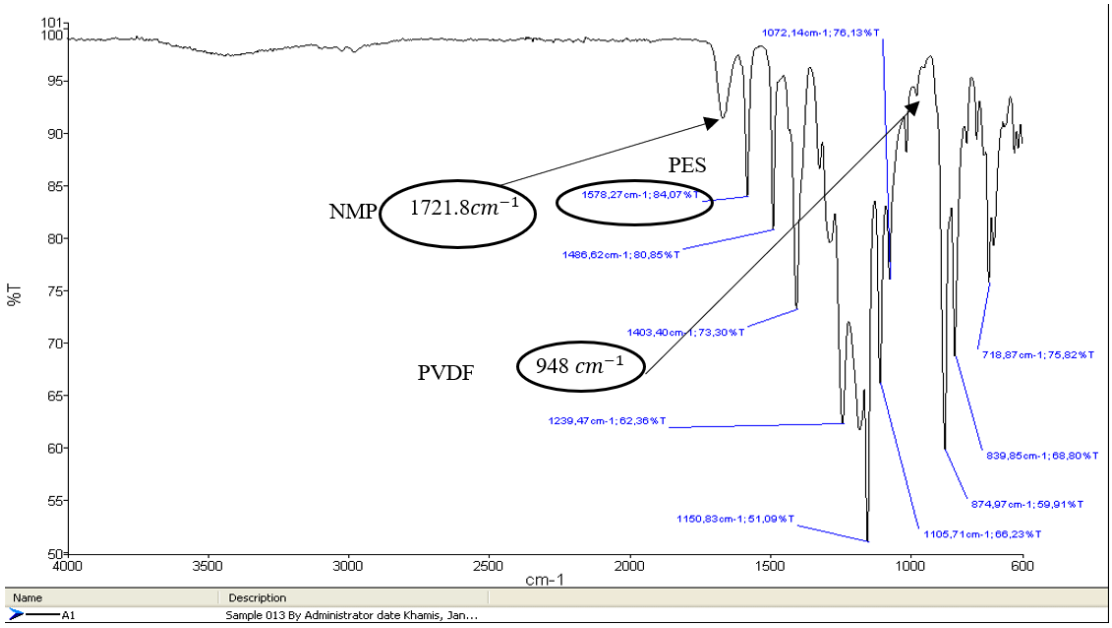


Figure 4: FTIR spectra of the a(i) membrane

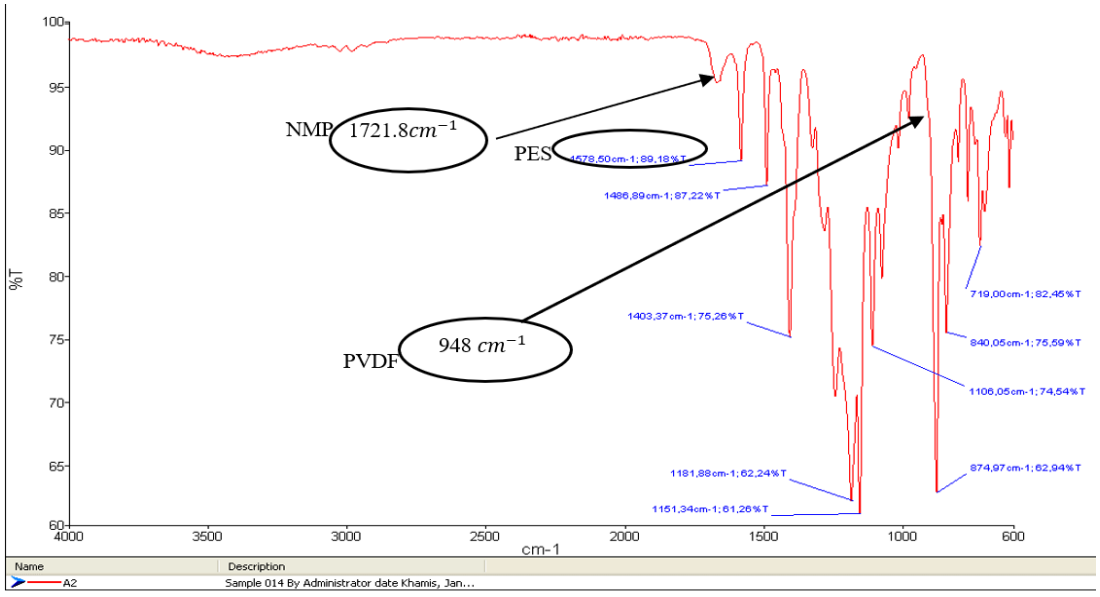


Figure 5: FTIR spectra of the a(ii) membrane

3.5 Analysis on permeate flux

Based on the table 2, for the pure water flux, the lowest flux was 7502.89 L/m^{2}h that resulted when using the b(i) that has no presence of GO for the concentration ratio of 1 : 1 of PVDF to PES. From the observation, the membrane that has not been added with GO has a lower flux compared to the one that has been added. This can be proof by the flux of membrane a(i) that was equal to 20834.20 L/m^{2}h and also the c (i) membrane that produced flux of 17153.25 L/m^{2}h.

Meanwhile for oily wastewater, the membrane that produced the lowest flux was the b(ii) which mean it has been added with GO and the value of flux was . 2472.93 L/m^{2}h. This trend was also acceptable for a(ii) membrane that also contributed in lower oily wastewater flux that was equal to 16511.46 L/m^{2}h. But it was slightly different to c (ii) membrane that produced a higher flux that was 25684.50 L/m^{2}h compared to c (i) that only produced 14665.77 L/m^{2}h.

Table 2: Membrane and flux

Membrane	Ratio PVDF to PES concentration	Flux(L/m^{2}h)	
		Pure water	Oily wastewater
a(i)	1 : 1	20834.20	22705.19
a(ii)	1 : 1	21014.58	16511.46
b(i)	2 : 1	7502.89	3299.79
b(ii)	2 : 1	9107.63	2472.93
c(i)	1 : 2	17153.25	14665.77
c(ii)	1 : 2	19653.32	25684.50

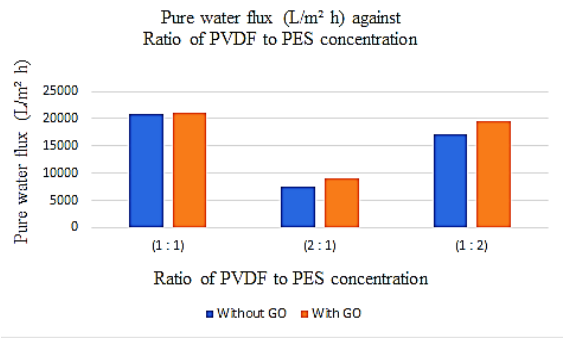


Figure 6 : Pure water flux against ratio PVDF to PES concentration time graph

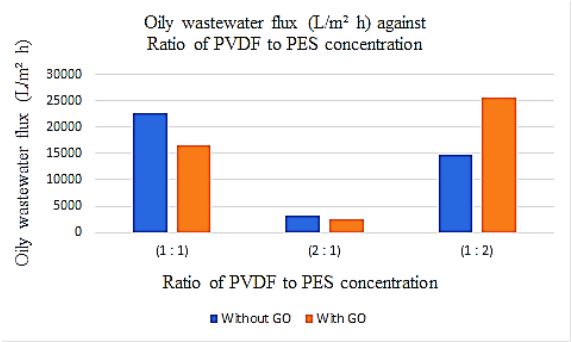


Figure 7 : Oli flux against ratio PVDF to PES concentration time graph

Furthermore, the figure 6 and 7 shown the graph of pure water flux against ratio PVDF to PES concentration and oily wastewater flux against ratio PVDF to PES concentration respectively. The trend of both graphs differed due to the varied feed solutions, which were pure water and oily wastewater solution. Both solutions have varying concentrations, which may influence the permeate flux value[10]. Thus, these graphs clarified the flux performance for all the membranes.

3.6 Analysis on oil rejection

Oil rejection has been calculated using equation 2, and the data needed was the concentration of the feed solution of oily wastewater, and for this study, the feed solution concentration was 1.903 ppm.

Table 3 shown the oil rejection percent after filter used those 6 different membranes. The highest oil rejection percent was 97.90% when used b(ii) membrane. This membrane was added with GO and with the 2: 1 PVDF to PES concentration ratio. The a(ii) membrane that also has been added with GO,

also has higher rejection compared to a(i) in which has no presence of GO and the percent of rejection was equal to 73.62%. This differ when using the c membrane, in which c(ii) that produced a lower rejection that was only 31.69% compared to c(i).

Table 3: Permeate concentration and oil rejection

Membrane	Ratio PVDF to PES concentration	Oil rejection, R (%)
a(i)	1 : 1	44.51
a(ii)	1 : 1	73.62
b(i)	2 : 1	89.81
b(ii)	2 : 1	97.90
c(i)	1 : 2	80.10
c(ii)	1 : 2	31.69

Next, the figure 8 shown the relationship between oil rejection percent with the ratio PVDF to PES concentration. The trend of this graph was the oil rejection will be higher if has been added with GO except for the c membrane. This might be due to the ratio of PVDF/PES blended membrane incorporated with GO at c(ii) was not really suitable for oil rejection.

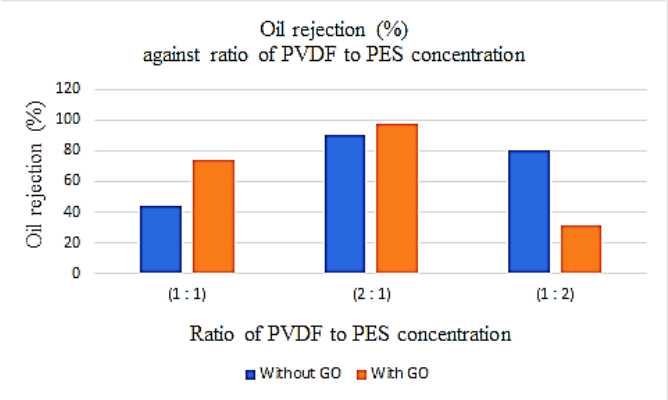


Figure 8: Oil rejection against ratio PVDF to PES concentration graph

4. Conclusion

The focus of this study is to fabricate PVDF/GO composite membrane and this was successfully achieved through NIPs method for treating oily wastewater. The next main objective in this study was characterized the chemical and physical properties of prepared composite membrane. The physical properties have been characterized using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The SEM images of the membrane was not clearly this was because it was not suitable magnification for the ultrafiltration. The AFM analysis of surface roughness resulted the lowest value of roughness was the membrane c(ii), 21.288 nm. Next, the physical properties of these membrane were characterized by using contact angle (CA) and Fourier Transform Infrared (FTIR). The hydrophilicity or hydrophobicity of the membrane were identified using CA study. The study shown the value of CA were increased when adding the GO. That might not be occurred because GO was one of the hydrophilic particle and might decrease the value of CA. But in this study, the result was vice versa. That was because of the concentration of GO was not high compared to PVDF. Then, the membranes also characterized using FTIR to get their chemical bonding. Finally, the oil rejection performance was calculated using specific equation after getting the data using the UV-Vis spectrophotometers. The highest oil rejection was 97.90% and the lowest oil flux were come from b(ii)

membrane with value 2472.03 Lm^2h. Thus, make it the best membrane and the best ration of PVDF to PES concentration which was 2 to 1.

Finally, even though this objective of study was achieved, there must a few improvements that can enhanced the rejection performance. Firstly, the concentration of the Graphene Oxide (GO) can be higher than 0.1 wt%. This is because it will increase the hydrophilicity of the membrane. Thus, improve the performance in rejecting oil for the oily wastewater. Next, to genuinely obtain real-world data on membrane performance, a more realistic simulation of the treatment should be developed. For this, industries should provide opportunities for researchers to test their treatment plants using industrial oily wastewater rather than laboratory oily wastewater.

Acknowledgement

The author wishes to express her heartfelt thankfulness to God for allowing this project report to be completed successfully. Ts. Dr. Norasyikin Binti Misdan, the author's supervisor, deserves special thanks for her warm support, inspiration, thoughtful guidance, advisement, and patience in helping me through this assignment. This acknowledgment would be incomplete without thanking the author's family members, the greatest source of energy. Blessings of author's parents, Mrs. Sh.Rohani Binti Syed Omar and Mr. Mohamed Bin Abd Karim this study would not be possible without the support from them. The authors would like to thank the Faculty of Engineering Technology, Universiti Tun Hussein Onn Malaysia for its support.

References

[1] Adetunji, A. I., & Olaniran, A. O. (2021). Treatment of industrial oily wastewater by advanced technologies: a review. Applied Water Science, 11(6). https://doi.org/10.1007/s13201-021-01430-4

[2] Kuyukina, M. S., Krivoruchko, A. V., & Ivshina, I. B. (2020). Advanced Bioreactor Treatments of Hydrocarbon-Containing Wastewater. Applied Sciences, 10(3), 831. https://doi.org/10.3390/app10030831

[3] Abuhasel, K., Kchaou, M., Alquraish, M., Munusamy, Y., & Jeng, Y. T. (2021). Oily Wastewater Treatment: Overview of Conventional and Modern Methods, Challenges, and Future Opportunities. Water, 13(7), 980. https://doi.org/10.3390/w13070980

[4] Shi, J., Huang, W., Han, H., & Xu, C. (2020). Review on treatment technology of salt wastewater in coal chemical industry of China. Desalination, 493, 114640. https://doi.org/10.1016/j.desal.2020.114640

[5] Siddique, T., Dutta, N. K., & Choudhury, N. R. (2021). Mixed-Matrix Membrane Fabrication for Water Treatment. Membranes, 11(8), 557. https://doi.org/10.3390/membranes11080557)

[6] Zhu, Y., Murali, S., Cai, W., Li, X., Suk, J. W., Potts, J. T., & Ruoff, R. S. (2010). Graphene and Graphene Oxide: Synthesis, Properties, and Applications. Advanced Materials, 22(35), 3906–3924. https://doi.org/10.1002/adma.201001068

[7] Hilal, N., Ismail, A. F., Matsuura, T., & Oatley-Radcliffe, D. (2019). Membrane Characterization (1st ed.). Elsevier.

[8] Montemor, M. F. (2018). Smart Composite Coatings and Membranes: Transport, Structural, Environmental and Energy Applications. Elsevier Gezondheidszorg.

[9] Misdan, N., Lau, W. Y., Ismail, A. F., & Matsuura, T. (2013). Formation of thin film composite nanofiltration membrane: Effect of polysulfone substrate characteristics. Desalination, 329, 9–18. https://doi.org/10.1016/j.desal.2013.08.021.

[10] Byrne, W. (2023). Reverse Osmosis 2nd Ed Second Edition (Second Edition). TO.