Fabrication and Characterization of Polysulfone Membrane Based On GO-SiO₂ Composite using Phase Inversion Method

Wineke Angesti, M. Munasir*

Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Surabaya, Ketintang Campus, Surabaya-East Java-Indonesia

Abstract. This research purpose to determine the material composition in the manufacture of polysulfone membranes by producing the best performance in the filtration application process. Polysulfone has good thermal and chemical stability properties that make it a candidate material in membrane manufacturing, but the hydrophobicity properties of polysulfone result in less than optimal membrane performance, so a blending process is needed to reduce hydrophobicity by maintaining the advantages of the membrane. The membrane was prepared using phase inversion with composite doping through the TEOS in situ hydrolysis method. The results of XRD identification showed that the diffraction pattern was successfully coated with silica with the amorphous phase, while the FTIR contained Si-O-Si bonds with a wave number of 1054 cm⁻¹. The SEM surface morphology showed that the presence of silica and GO made the pore size larger with the pore size on the membrane 1,92 μm. The results of the contact angle test on the GO-SiO₂/PSF variation of 0,8 obtained the lowest hydrophobicity value of 70,17°. The addition of composites will result in a larger pore size supported by the value of the contact angle, proving that the combination of the composite in polysulfone can increase the hydrophilicity of the membrane.

Keywords: Polysulfone Membranes, GO-SiO₂, Hydrolysis Method

1 Introduction

The provision of clean water is becoming an increasingly important issue in line with population growth, especially in coastal areas. This problem is very significant where clean water sources are increasingly scarce. The scarcity of clean water sources is due to the fact that nearly 97,5% of the water on earth is water with a salt content found in the ocean and the remaining 2,5% is fresh water in the areas of rivers, icebergs, land and lakes which cover most of the needs of living things [1]. Sea water with high salt content can be used as an alternative solution in meeting the needs of clean water by separating the dissolved salt content in the water through a desalination process. Desalination technology has been used in recent years around the world to produce clean water from seawater to improve the quality of clean water supplies as a source of human consumption [2].

Technological developments have resulted in breakthroughs in clean water treatment including membrane desalination. Membranes are an important part of the desalination process which makes it possible to remove dissolved species such as salts, organic compounds, colloidal solids, suspension solids, bacteria, and viruses that cannot be removed by other technologies [3], [4]. Polysulfone is a polymer that can form asymmetric membranes and is widely used as a basis for making membranes for commercial

microfiltration, ultrafiltration, nanofiltration and reverse osmosis because it has good thermal, mechanical and chemical stability properties [5], [6]. The application of polysulfone membranes is still very limited because of its hydrophobic nature which is always associated with low membrane permeability [7]. The permeability of this membrane can be increased by the addition of hydrophilic particles such as GO and SiO₂ to the polysulfone membrane so that it will result in an increased ability of membrane hydrophilicity[8].

Graphene oxide is a material commonly used in preparing membranes because it has unique properties, such as, high surface area, thermo-mechanical stability and hydrophilic properties with high chemical activity which will form a regular dispersion in water, therefore it is used as a material in water. membrane modification [9], [10]. GO has a functional hydrophilic group with oxygen content which will result in high hydrophilicity so that it will result in optimal material properties in the membrane[11]. The combination of graphene oxide with silica will increase, hydrophilicity, permeability and anti-fouling ability as well as the presence of salt rejection on the membrane by 99,99%[12], [13]. SiO₂ is an inorganic material that has excellent thermal, chemical stability and also high hydrophilic properties so it is used as a material in the manufacture of membranes, this hydrophilic nature can prevent fouling by increasing membrane permeability[14]. Silica particles with a smaller size have a greater ratio of

*Corresponding Author: munasir_physics@unesa.ac.id

external surface area to volume value, which will increase the performance of the membrane [15].

Research [8] reports that, using GO-SiO₂ composites as a membrane building material will produce the best hydrophilicity which contributes to an increase in water permeability in the membrane, compared to the absence of silica and graphene oxide composites, resulting in less than optimal hydrophilic properties that will result in less than optimal hydrophilic properties. reduce membrane permeability. Based on the results of these descriptions, this research is a development of research [10]. The research was conducted by synthesizing GO-SiO₂ composites with the Hummer method to produce a uniform composite on the membrane. The process of making membranes in previous research was carried out through the phase inverse method using the constituent material of SiO₂-GO/MCE, this motivated researchers to optimize previous research by varying the constituent material of the membrane using GO-SiO₂/PSF. It is hoped that the presence of a polysulfone membrane will show significant advantages in the membrane application process

2 Materials and Methods

2.1 Materials

The materials used are graphite powder obtained from coconut shell extract, potassium permanganate (KmnO₄, 99%), sodium nitrate (NaNO₃), hydrogen peroxide (H₂O₂, 30%), ammonia (NH₄OH, 25%), tetraethyl orthosilicate (TEOS) and distilled water all of which were obtained from SIP, Ethanol (C₂H₅OH, 99.7%) was obtained from Edu Lab, Hydrochloric acid (HCL, 37%) was obtained from Mallinckrodt, Sulfuric acid (H₂SO₄, 95-97%) was obtained from Indofa, NMP obtained from Merck, and polysulfone (PSF, MW 35,000) recovered from Sigma Aldrich.

2.2 Methods

2.2.1 Synthesis of graphene oxide

Synthesis of GO using the hummer method where 5 grams of graphite powder and 2,5 grams of NaNO₃ powder are dissolved in 120 mL of sulfuric acid under ice bath conditions and stirred for 30 minutes with a magnetic stirrer. 15 grams of KmnO₄ are added slowly in the solution and stirred at a temperature below 20° C for 30 minutes until the solution turns purple. After that, continue stirring for 3 hours at room temperature. After the solution turned brown, 150 mL of distilled water was added and the temperature was adjusted to 95° C for 3 hours. After the brownish yellow solution is formed, 50 mL of 30% peroxide solution is slowly added to remove the manganate compound, the solution is washed with 1 M HCL and distilled water until neutral followed by drying at 60° C for 6 hours.

2.2.2 Synthesis of GO-SiO₂ composite

Synthesis on GO-SiO₂ composites using TEOS in situ hydrolysis method. 12,5 mg GO was dispersed in 150 ml of ethanol-distilled water with a ratio of 1: 5 and sonified for 30 minutes. The pH of the reaction mixture is adjusted close to 9 with the addition of ammonia. 0,6-1,2 mL TEOS were added to the solution and reconfirmed for 30 minutes. After that the mixture was stirred for 24 hours at room temperature then the solution was centrifuged and washed using ethanol followed by a drying process at 60° C for 12 hours.

2.2.3 Fabrication GO-SiO₂/PSF Membrane

GO-SiO₂/PSF membrane fabrication was carried out using the phase inversion method where 1 gram of polysulfone was mixed in 5,469 mL NMP and stirred for 3 hours until the solution was homogeneous. 0,0333 grams of GO-SiO₂ composite was added to a homogeneous solution to produce a solution of 0,5 wt%, then the solution was sonicated for 30 minutes to speed up the dissolving process without any air bubbles in it. The solution formed is printed on a glass plate and immersed using distilled water for 24 hours after which the drying process is carried out at room temperature for 24 hours.

Fig. 1. GO-SiO₂/PSF membrane fabrication chart

2.3 Characterization

The X-Ray Diffraction (XRD) test was used to detect crystalline compounds in the GO-SiO₂ sample that had been synthesized (Philips type X'pert Analytical XRD with CuK α radiation source). Fourier-transform infrared spectroscopy (FTIR) testing was used to identify functional groups in GO-SiO₂ composite samples (Shimadzu type IR One 8400S). Scanning Electron Microscopy testing is treated to determine the morphology of the membrane surface material (FEI type Inspect-S50). The contact angle test was used to measure the hydrophilicity of the GO-SiO₂/PSF membrane (Goniometer type LSB-1800B).

Fig. 2. Membrane contact angles displayed by Matlab-software

Measurement of the contact angle was carried out using the sessile drop method by dripping convex water on the surface of the substrate and measuring the angle between the water droplets and the membrane surface using a goniometer, and the results obtained from the measurements were displayed through the Matlab software.

Figure 2 shows that when the energy of the interface in the liquid and gas is in contact with the solid surface, it will produce three interface forces on the solid-liquid, gas-liquid and solid-gas substance. The presence of this force will cause an equilibrium generated by the contact angle through Young's equation [16]:

$$\cos \theta = \frac{\gamma_s - \gamma_{sl}}{\gamma_l} \quad (1)$$

Where γ_s is the solid-gas surface interface tension, γ_{sl} is the solid-liquid interface tension and γ_l is the gas-liquid interface tension, while θ is the formed contact angle.

3 Results and discussion

3.1 XRD GO-SiO₂ composite

The crystal structure of the GO-SiO₂ composite that was synthesized together with SiO₂ and GO particles was determined using the diffraction method using XRD as shown in Figure 3.

Fig. 3. X-ray diffraction pattern on graphite, GO and GO-SiO₂ composites.

The crystal structure of GO-SiO₂ showed diffraction peaks at $2\theta = 20.70^\circ$, 21.81° , 26.48° and 27.65° correspond to the crystal plane (100), (002), (101) and (220) respectively. The prominent and common peaks appearing around 21.81° in GO-SiO₂ and GO composites are associated with the (002) crystal field of graphene oxide [17], [18]. Significantly, the GO-SiO₂ composite shows a wide and sloping surface at an angle of 23.52° this is due to the amorphous surface structure of SiO₂. The results of this study are in accordance with research conducted by [19] where Graphene/SiO₂ composites were successfully formed at the diffraction peaks of $2\theta \sim 20^\circ$ - 30° .

3.2 FTIR GO-SiO₂ composite

The FTIR spectrum is used to identify the wave absorption pattern in Graphite, GO and GO-SiO₂ samples as shown in Figure 4.

Fig. 4. FT-IR spectrum graph of the composite Graphite, GO and GO-SiO₂

The spectrum in the GO-SiO₂ composite with absorption peaks at 1054 cm^{-1} and 795 cm^{-1} , respectively representing the asymmetric and symmetric vibrations of the Si-O-Si bonds, this indicates that the GO surface was successfully mixed with SiO₂ in the GO-SiO₂ composite. The spectral peaks indicated at wave numbers 1020 cm^{-1} , 3212 cm^{-1} and 1581 cm^{-1} are respectively C-O bond stretching vibrations, -OH bond stretching vibrations and C = C bond stretching vibrations. In addition, the typical intensity of the absorption peak indicated at 1710 cm^{-1} was the vibration of the C=O carboxylate group. From these data, it can be seen that the functional groups on GO-SiO₂ show an absorption peak that is similar to the functional groups owned by GO and graphite.

3.3 GO-SiO₂/PSF membrane morphology

The membrane was prepared using the phase inverse method and characterized by a scanning electron microscope (SEM) to determine the surface morphology of the membrane. The results in Figure 5 (a-b) show the surface morphology of GO and GO-SiO₂ membrane pores. The image is then used in analyzing the pore size using Image-J software. The surface of the membrane showed that the pore size was not uniform with the number of pores that were irregular in both GO and GO-SiO₂ membranes, the pore diameter sizes on each membrane ranged from 44 nm-943,44 nm and 234,37 nm-1,92 μm . The results of measuring the pore diameter on the membrane show that the GO membrane is classified as a nanofiltration material, while the GO-SiO₂ membrane is an ultrafiltration membrane. The pore size in the membrane leads to the large fraction of the volume of the empty space between the pores for water storage. The larger the membrane pore size, the smaller the pressure required to push the bait through the membrane, compared to the small pore size requiring greater pressure, this happens because the smaller pore

size requires high pressure so that the bait can pass through the membrane [20].

Fig. 5. SEM of membrane surface with magnification of 10,000x (a) GO and (b) GO-SiO₂.

The membrane surface which is not observed from Figure 5(a) shows that in the absence of SiO₂ the pore size of the membrane is smaller and less uniform than that of the non-uniform membrane. Figure 5(b) shows that by adding silica and graphene oxide in the membrane composition, the resulting pore size is larger and more regular. From these results, it can be seen that the addition of GO-SiO₂ composites will have an impact on increased pore size and distribution, this is in accordance with the study [8].

In the SEM images of each membrane there is a white lump caused by agglomeration of GO and SiO₂ particles on the membrane, so that the distribution of particles is uneven. This is due to the imperfect sonication process of the composites in the fusion process, which leads to clumps on the membrane.

3.4 GO-SiO₂/PSF membrane contact angle

The contact angle is a measurement of the surface wetness of the substrate to determine the hydrophilicity or hydrophobicity which will affect the performance of the membrane. The membrane is said to be hydrophilic, if it has a contact angle value ($0^\circ < \theta < 90^\circ$). As it is known, a lower contact angle indicates greater hydrophilicity. The increase in the hydrophilicity of the

membrane surface has the potential to reduce the tendency of fouling (clogging) to the membrane.

Fig. 6. Graph of membrane contact angles with doping PSF, GO-SiO₂/PSF (0.6, 0.8, 1.0, 1.2) and SiO₂/PSF

Based on the description above to determine the hydrophilicity of the membrane, the measured contact angles are presented in Figure 6. The PSF membrane has the highest contact angle (80,25°) however, the surface contact angle decreases after the incorporation of GO-SiO₂ composites on the PSF membrane with the lowest contact angle value (70,17°). This suggests that composite doping increases membrane hydrophilicity. Compared to pure SiO₂/PSF and PSF membranes, the addition of GO-SiO₂ produces a larger hydrophilic membrane, this is due to the polarity of functional groups, namely epoxy, hydroxyl, carboxyl and siloxane which enter the membrane surface [21]. The addition of GO-SiO₂ composites to the membrane will reduce the surface foulant interaction so that it will reduce the occurrence of fouling in the membrane[12]. The results obtained from sample 1 to sample 4 indicate that the hydrophilicity increases with the increase in GO-SiO₂ content, but in samples 5 and 6 the hydrophilicity value decreases this is due to the presence of agglomeration in the membrane.

4 Conclusions

The results of the x-ray diffraction characteristics were successfully formed by the presence of an amorphous silica diffraction pattern on the GO-SiO₂ composite and the FTIR spectrum showed an asymmetrical vibration of Si-O-Si, this indicated that the GO surface was successfully mixed with SiO₂. The addition of graphene oxide and silica composites will increase the hydrophilicity at the contact angle by 14,36%, while the SEM surface morphology shows that the presence of GO-SiO₂ mixed composites on the polysulfone membrane will result in larger and more uniform pore sizes, so that the results of this study prove that the GO-SiO₂/PSF membrane as a candidate material that can be applied as a water filter.

References

- [1] M. Thimmaraju, D. Sreepada, G. S. Babu, B. K. Dasari, S. K. Velpula, and N. Vallepu, "Desalination of Water," p. 16, (2018).
- [2] R. A. Nugroho, H. Ma'rufah, L. M. Khusna, Y. Wahyono, and H. Sutanto, "Seawater desalination using distillation method based on convex lens and Ag doped ZnO thin film to improve freshwater productivity and quality," *IOP Conf. Ser.: Earth Environ. Sci.*, vol. **243**, p. 012120, Apr. (2019), doi: 10.1088/1755-1315/243/1/012120.
- [3] L. Chen, P. Xu, and H. Wang, "Interplay of the Factors Affecting Water Flux and Salt Rejection in Membrane Distillation: A State-of-the-Art Critical Review," *Water*, vol. **12**, no. 10, p. 2841, Oct. (2020), doi: 10.3390/w12102841.
- [4] M. R. Jamalludin *et al.*, "The Effect of Hydrophilicity of Graphene Oxide as Additive Towards Performance of Polysulfone Membrane," p. 7, (2017).
- [5] A. Ammar, Al-Enizi, Abdullah M, Almaadeed, Mariam Alali, and Karim, Alamgir, "Influence of graphene oxide on mechanical, morphological, barrier, and electrical properties of polymer membranes," p. 13, (2016).
- [6] D. Ma, Z. Wang, T. Liu, Y. Hu, and Y. Wang, "Spray coating of polysulfone/poly(ethylene glycol) block polymer on macroporous substrates followed by selective swelling for composite ultrafiltration membranes," *Chinese Journal of Chemical Engineering*, vol. **29**, pp. 85–91, Jan. (2021), doi: 10.1016/j.cjche.2020.05.002.
- [7] H. T. V. Nguyen *et al.*, "Preparation and Characterization of a Hydrophilic Polysulfone Membrane Using Graphene Oxide," *Journal of Chemistry*, vol. **2019**, pp. 1–10, Jun. (2019), doi: 10.1155/2019/3164373.
- [8] M. B. Alkindy, V. Naddeo, F. Banat, and S. W. Hasan, "Synthesis of polyethersulfone (PES)/GO-SiO₂ mixed matrix membranes for oily wastewater treatment," *Water Science and Technology*, vol. **81**, no. 7, pp. 1354–1364, Apr. (2020), doi: 10.2166/wst.2019.347.
- [9] A. T. Smith, "Synthesis, properties, and applications of graphene oxide/reduced graphene oxide and their nanocomposites," p. 17, (2019).
- [10] J. Sun, H. Bi, S. Su, H. Jia, X. Xie, and L. Sun, "One-step preparation of GO/SiO₂ membrane for highly efficient separation of oil-in-water emulsion," *Journal of Membrane Science*, vol. **553**, pp. 131–138, May (2018), doi: 10.1016/j.memsci.2018.02.029.
- [11] F. Wang, Y. Wu, and Y. Huang, "Novel application of graphene oxide to improve hydrophilicity and mechanical strength of aramid nanofiber hybrid membrane," *Composites Part A: Applied Science and Manufacturing*, vol. **110**, pp. 126–132, Jul. (2018), doi: 10.1016/j.compositesa.2018.04.023.
- [12] Y. Liu *et al.*, "A multifunctional hierarchical porous SiO₂/GO membrane for high efficiency oil/water separation and dye removal," *Carbon*, vol. **160**, pp. 88–97, Apr. (2020), doi: 10.1016/j.carbon.2020.01.002.
- [13] Y. Mao *et al.*, "Roughness-enhanced hydrophobic graphene oxide membrane for water desalination via membrane distillation," *Journal of Membrane Science*, vol. **611**, p. 118364, Oct. (2020), doi: 10.1016/j.memsci.2020.118364.
- [14] H. P. Ngang, A. L. Ahmad, S. C. Low, and B. S. Ooi, "Preparation of PVDF/SiO₂ composite membrane for salty oil emulsion separation: Physicochemical properties changes and its impact on fouling propensity," p. 12, (2016).
- [15] A. Martín, J. M. Arsuaga, N. Roldán, J. de Abajo, A. Martínez, and A. Sotto, "Enhanced ultrafiltration PES membranes doped with mesostructured functionalized silica particles," *Desalination*, vol. **357**, pp. 16–25, Feb. (2015), doi: 10.1016/j.desal.2014.10.046.
- [16] A. Kumarasiri, D. A. S. Amarasinghe, and D. Attygalle, "Surface Wettability Analysis of Nichrome Alloy Based on the Measurements of Sessile Droplet Contact Angles," p. 6, (2020).
- [17] P. V. Shitre, R. R. Harale, B. R. Sathe, and M. S. Shingare, "Silica nanosphere-graphene oxide (SiO₂-GO) hybrid catalyzed facile synthesis of functionalized quinoxaline derivatives," *Res Chem Intermed*, vol. **43**, no. 2, pp. 829–841, Feb. (2017), doi: 10.1007/s11164-016-2667-8.
- [18] G. Wu, L. Ma, L. Liu, L. Chen, and Y. Huang, "Preparation of SiO₂-GO hybrid nanoparticles and the thermal properties of methylphenylsilicone resins/SiO₂-GO nanocomposites," *Thermochimica Acta*, vol. **613**, pp. 77–86, Aug. (2015), doi: 10.1016/j.tca.2015.05.026.
- [19] M. Munasir and M. Dayu, "Graphene/SiO₂ Nanocomposite From Natural Material," presented at the Proceedings of the 7th Mathematics, Science, and Computer Science Education International Seminar, MSCEIS 2019, 12 October 2019, Bandung, West Java, Indonesia, Bandung, Indonesia, (2020). doi: 10.4108/eai.12-10-2019.2296373.
- [20] J. Prawira, "Karakteristik Membran Dan Pengaruhnya Terhadap Kinerja Proses Distilasi Membran," Dec. (2017), doi: 10.5281/ZENODO.1134034.
- [21] R. W. Kibechu, D. T. Ndinteh, T. A. M. Msagati, B. B. Mamba, and S. Sampath, "Effect of incorporating graphene oxide and surface imprinting on polysulfone membranes on flux, hydrophilicity and rejection of salt and polycyclic aromatic hydrocarbons from water," *Physics and Chemistry of the Earth, Parts A/B/C*, vol. **100**, pp. 126–134, Aug. (2017), doi: 10.1016/j.pce.2017.01.021.