Hydrophobicity Properties of Graphite and Reduced Graphene Oxide of The Polysulfone (PSf) Mixed Matrix Membrane


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ABSTRACT

Hydrophobicity properties of graphite and reduced graphene oxide (rGO) (from exfoliated graphite/rGO) towards PSf polymer membrane characteristic and properties at different additives weight concentrations (1, 2, 3, 4, and 5 wt. %) were investigated. Both PSf/graphite and PSf/rGO membranes were characterized in term of hydrophobicity, surface bonding, surface roughness and porosity. FTIR peaks revealed that membrane with graphite and reduced graphene oxide nearly diminished their O-H bonding which was opposite to the graphene oxide peak that shows a strong O-H bonding as increased exfoliated times. These results were in line with the contact angle results that showed strong hydrophobicity of graphite and reduced graphene oxide membranes as increased these additives concentration. The effect of strong hydrophobicity in these membranes also has resulted in smoother surface roughness compared to pristine PSf membrane. Further investigation of the performance of water flux also proved that both above membranes have strong hydrophobic effect, with the lowest pure water flux rate (L/m² h) was given by PSf/rGO 3% membrane at 19.2437 L/m² h.


NOMENCLATURE

- ρ: Pure water density (g/cm³)
- v: Membrane volume in wet state (cm³)
- rm: Mean pore size value
- η: Water viscosity (8.9 x 10⁻⁴ Pa S)
- Q: Permeate water volume per unit time (m³/s⁻¹)
- PWF: Pure water flux
- t: Time (h)
- W_d: Dried weight (g)
- W_w: Wet weight (g)
- E: Porosity
- L: Membrane thickness (m)
- A: Membrane effective area (m²)
- Q: Permeate volume (L)

1. INTRODUCTION

Most of the recent industrial activity such as food, palm oil extraction, oil and gas, transportation generate of high oily waste effluent which is not easily to be treated and eliminated. The oily wastewater is categorized as strong polluted solution which is required special treatment and normally involved many steps of treatment and purification. In fact, such contaminants are harmful to the nature ecosystem and wild life, environmental, human health and degrade the energy generation [1, 2, 3]. Thus, separation of oily wastewater solution contaminant is considered as a crucial technology that need to be developed to ensure the sustainability of recent industries as well as the nature ecosystem. Conventionally, the treatment or separation processes use physical adsorption, chemical degradation, membrane separation, gravity separation...
and many more [2, 4, 5] that involves very complex step and routes. In fact, this traditional techniques for oil wastewater separation showed slightly high in cost of treatment and low efficiency [3]. Thus, membrane separation with simple operational and high quality output is preferred to be used in treating oily waste medium. Previous study by Padaki et al. [6] has revealed that the membrane technology is able to provide an efficient technique to separate the oil-water mixture based on their ability in separating different compound based on the size of molecule and pollutants along together with their high selectivity due to membrane materials properties.

In fact, membrane technology is used until now for separating most the complex solution or mixture [7]. One of the most frequently used polymer is polysulfone (PSf) that has strong hydrophobic properties in nature [8, 9]. Previous study by Ficai et al. [10] reported that the fabrication of PSf membrane can be produced with a very small pore size until down to 0.2 μm or less. Also, PSf membrane is always known due to its excellent performance compared other polymer membrane [10] such as a low cost, high chemical compatibility, good heat resistance, easy processability, and resistance over a wide range of pH.

Recently, membrane technology with strong hydrophobic properties is widely used for oily medium. As revealed by previous study by Akin et al. [11] mentioned that carbon-based nanomaterials such as fullerene, carbon nanotube and graphene have been successfully incorporated with PSf membrane with strong hydrophobic effect. Since, graphite and graphene are generally hydrophobic in nature and their properties are limited in water separation application. In fact, the graphite structure showed that the presence of strong covalent bonds between the carbon atoms in each layer and weaker forces that hold the layers together [12], [13]. Meanwhile, graphene oxide (GO) is a single-atomic layered material comprising carbon, hydrogen, and oxygen molecules [14] and has the ability slightly easily dispersed in water compared to graphites due to limitation in getting graphene materials. Thus, GO is used to produce the graphene in this study. The reduction of GO involve the removal of oxygen-containing groups and with the recovery of a conjugated structure. From this reduction step, the graphene-like sheets is produced with slightly increased of hydrophobic property [8].

2. MATERIALS

2. 1. Reduced Graphene Oxide (rGO) In this study, graphene oxide (GO) was synthesized via hummers’ method. Graphite powder was purchased from Aldrich (<20 μm, synthetic). Sulphuric acid (H₂SO₄, QRec) and phosphorus acid (H₃PO₄, QRec) were used as solvent to mix graphite homogenously. Meanwhile, potassium permanganate (KMnO₄, Bendosen), hydrogen peroxide (H₂O₂, QRec) and deionized water was used together as reducing agents [15]. Reduced graphene oxide (rGO) was prepared by using local curry leaf extract as the green reducing agent.

2. 2. PSf/Graphite and PSf/rGO Membrane Preparation Polysulfone (PSf) pellets was purchased from Sigma Aldrich while N-Methyl-2-Pyrrolidone (NMP, QRec) was used as solvent. In this work, graphite and reduced graphene oxide (rGO) powders were reacted to be used as additives. Polyethylene glycol (PEG, QRec) was used as a membrane pore former.

3. METHODOLOGY

3. 1. Graphene Oxide (GO) Preparation The preparation of GO was performed using Hummers’ method [18]. 5 g of graphite, 108 ml of sulphuric acid (H₂SO₄), 12 ml of phosphorus acid (H₃PO₄) and 2.5 g of sodium nitrate were mixed in a beaker. Then, the solution was stirred in an ice bath until the temperature reached 15 °C. After 1 hour, 15 g of potassium permanganate (KMnO₄) was slowly added into the solution and continuously stirred until temperature reached 20 °C to 30 °C. At 30 °C, 140 ml of the deionized water was added into the solution and stirred for 1 hour. 15 ml of hydrogen peroxide (H₂O₂) was added into the solution half an hour before completion. The solution was washed several times with distilled water until pH 7 was obtained [17, 19]. Next, GO was exfoliated by ultra-sonication of the solution for 1 hour.

3. 2. Reduced Graphene Oxide (rGO) The reduced graphene oxide (rGO) was synthesized using a curry leaves extract as a green reducing agent. Firstly, 20 ml of curry extract was boiled in a range 60 °C to 80 °C [18]. Next, 100 ml of GO solution was mixed together with curry leaf extract. Then, the solution was stirred at 95 °C for 12 hours. After that, rGO solution was centrifuged at 7,000 rpm for 10 min and washed for several times with distilled water to remove any un-exfoliated graphite oxide [19]. Finally, the rGO solution was dried in the oven at 70 °C [20]. Figure shows the mechanism route of graphite, graphene oxide (GO), and reduced graphene oxide (rGO).

3. 3. PSf/Graphite and PSf/rGO Membrane Preparation PSf/graphite and PSf/rGO membrane was fabricated via phase inversion method [8].
Graphite and rGO powder were used at different concentration (0, 1, 2, 3, 4 and 5 wt. %) in PSf polymer mixed matrix membrane.

3. 4. Characterization of Graphene Oxide (GO) and Reduced Graphene Oxide (rGO) Powder

Particle bonding of the synthesized graphite, graphene oxide (GO) and reduced graphene oxide (rGO) powder were investigated by Spectrum One FTIR Spectrometer (PerkinElmer). First, powders were prepared in dry environment. Then, the measurement was conducted in ranges 1000 cm⁻¹ until 4000 cm⁻¹. Comparison of the results with the standard previous peak is able to ensure the ability of the synthesis process of GO [21].

3. 5. Characterization and Performance of PSf/Graphite and PSf/rGO Membranes

3. 5. 1. Surface Roughness

Atomic force microscopy (AFM) was used to measure the surface roughness of PSf/graphite and PSf/rGO membrane at a high resolution. These samples were cut at 2 cm x 2 cm. These samples were placed on the glass slide and positioned on the top of scanner tube. The shiny surface of membranes were used as a main surface in the analysis. The AFM laser beam was absorbed on the spot area to illustrate the value of the root-mean-squared (Rq), mean roughness parameter (Ra) and the average roughness’s point (Rz) were determined using by XEI software [22]. However, The mean surface roughness (Ra) was selected as a result.

3. 5. 2. Porosity and Mean Pore Size (rm)

Membrane porosity was evaluated in percentage (%). Prior to the analysis, these samples were cut at 2 cm x 2 cm square. Then, these samples were soaked in water for 24 hours. After that, samples were measured the wet weight (Ww) by an electronic balance. Afterwards, membrane samples were dried in the oven at 50 °C for 24 hours. Then, the dried weight (Wd) of samples were measured. Previous study by Riduan et al. (2013) reported that the Guerot-Elford-Ferry equation was used to prove the porosity value [23].

\[
\text{Porosity, } \varepsilon = \frac{W_w - W_d}{\rho_w V}
\]  

\(\rho_w\) is called as pure water density at a room temperature (g/cm³) and V is stated as membrane samples volume in wet state (cm³). From the porosity test, i.e filtration velocity method, the value of mean pore size (rm) was determined.

\[
rm = \frac{(2.9-0.75\varepsilon) \times 89Q}{\varepsilon \times A \times \Delta t}
\]

3. 5. 2. Hydrophobicity Determination

The hydrophobicity of PSf/graphite and PSf/rGO membrane were determined by means of contact angle measurement. Membrane samples were prepared at 5 cm x 2 cm rectangular. Hydrophobicity was detected with contact angle more than 90 degree as reported by most of the previous researcher. Basically, hydrophobicity is defined as the condition whereby water is not easily absorb to the membrane surface. Thus, opposed condition when contact angle value less than 90 degree was categorized as hydrophilicity [24].

3. 5. 3. Pure Water Flux (PWF)

Pure water flux (PWF) of PSf/graphite and PSf/rGO membrane performance were measured via water permeation test. Pressure was selected at 2 bars and the permeation testing was conducted for 10 minutes. Then, PWF was measured according to the following equation [25,26].

\[
PWF = \frac{Q}{A \times \Delta t}
\]

4. RESULTS AND DISCUSSION

4. 1. Surface Bonding of Graphite, Graphene Oxide (GO) and Reduced Graphene Oxide (rGO)

Error! Reference source not found. shows the FTIR spectrums for the peak of graphite, graphene oxide (GO) and reduced graphene oxide (rGO) powder. Figure 1 (a) shows the GO synthesized powder with the existence peak of O-H stretching bond at 3317 cm⁻¹, indicating the hydrophilicity effect is slightly increased as compared to the main substrate graphite. Meanwhile, Figure 1 (b) shows the reduction of rGO which was confirmed with the significant reduction of strongest absorption band at 1713 cm⁻¹. The strong –OH peak located at 1151 cm⁻¹ for GO spectrum bonding was disappeared at rGO spectrum bonding, which is revealed to the reduced GO; that was successful conducted by curry leaf extract. Previous studies proved that the bonding of –OH peak was slowly disappeared after the reduced mechanism during the reduction process of GO [27].
Figure 1. FTIR spectrum of graphite, graphene oxide (GO) and reduced graphene oxide (rGO) powder

4.2. Surface Roughness of PSf/Graphite and PSf/rGO Membranes Surface roughness of PSf/graphite and PSf/rGO membranes are shown in Figure 2 and 4, respectively. The table shows the value of mean surface roughness parameters (Ra). The lowest mean surface roughness value (Ra) was given by PSf/rGO (5%) membrane at 15.042 nm. Then, followed by PSf/graphite (5%) membrane as the second lower of surface roughness with value at 15.477 nm. The lowest surface roughness might be related to the delay demixing process that occurred due to the increased of hydrophobic properties as proved in the FTIR spectrum. This was obviously shown by strongest hydrophobic rGO membrane which has the lowest surface roughness revealed the strong hydrophobic effect. The similar effect can be observed in both graphite and rGO membranes. As increased the concentration of graphite and rGO, the hydrophobicity of membrane also increased indicating that hydrophobicity play a role in influencing the delay phase inversion process. In this study, the lower surface roughness might be related to the lower porosity that appeared on the external surface of the membrane. Riduan et al. [25] revealed that the increased surface roughness was related to the higher porosity on the external surface of membrane. Furthermore, surface morphology of membranes at

4.3. Porosity and Mean Pore Size The porosity and the mean pore size were analyzed and measured for both PSf/graphite and PSf/rGO membranes samples with different concentration of graphite and reduced graphene oxide (rGO) embedded on the membrane (0, 1, 2, 3, 4 and 5 wt. %). Basically, membrane porosity can be defined as weight of pure water trapped in 1 m³ of membrane structure and is a very important parameter in membrane separation because it determines the membrane performances and properties [25]. Figures 6 and 7 show the porosity results of PSf/graphite and PSf/rGO membrane respectively. Meanwhile, Figure 7 and 9 show the mean pore size of PSf/graphite and PSf/rGO membrane. These results revealed that with higher value of porosity (ε) would result in the lower value of mean pore size (rm) for both types of membrane.

Figure 2. Mean surface roughness (Ra) results of PSf/graphite membrane

Figure 3. Mean surface roughness (Ra) results of PSf/rGO membrane
Increasing the amount of synthesized powder in both types of membrane the effect hydrophobicity also increases that result in the formation of bigger finger-like structure at top surface as shown by the increment of the mean pore size. The effect of hydrophobicity was slightly reduced at higher concentration that could be due to agglomeration effect that was shown by increasing porosity and reducing of mean pore size value. The value of mean pore size of PSf/rGO 1% membrane was reduced as the formation of finger-like structure becoming smaller at top surface. Overall the PSf/rGO membrane showed the lowest porosity value at all concentration of membrane that can be linked to the hydrophobicity of rGO powder.

4. 3. Contact angle Test of PSf/Graphite and PSf/rGO Membranes Graphite powder or particles consist of carbon atoms without polarity characteristic which create the tendency of hydrophobic properties [27]. Thus, the effect of synthesized powder towards this property in both types of membrane was measured using contact angle measurement. Contact angle values higher than 90° show the tendency of material to be in hydrophobic conditions.
Figure 9 and Figure 10 show the contact angle of PSf/graphite and PSf/rGO membranes, respectively. PSf/rGO (5%) membrane gives the highest of water contact angle value at 107.5°. This result revealed the strong hydrophobic of PSf/rGO (5%) compared to PSf/graphite membrane. As the concentration of synthesized powder increased the hydrophobicity also increased but slightly reduced for the PSf/graphite that may due to the agglomeration effect of graphite. Whereas PSf/rGO (1%) membrane shows less hydrophobic than PSf/graphite (1%) membrane; that could be due to small particles size have small effect which cannot significantly influence the bigger size of membrane. As the concentration of reduced graphene oxide (rGO) on membrane increased the hydrophobicity effect is obviously shown in this membrane. In addition, graphene oxide has a lot of oxygen containing functional groups compared to reduced graphene oxide (rGO) [27], but these results on PSf/rGO membrane showed the higher hydrophobic tendency as compared to graphite.

4.4. Water Permeability Test

Figure 11 and Figure 12 show the values of pure water flux rate (L/m²h) of PSf/graphite and PSf/rGO membrane at different concentrations (0, 1, 2, 3, 4 and 5 wt. %) of additive powder.

Basically, water permeability mechanism can be influenced by the effect of hydrophilicity and hydrophobicity of added particles into the membranes structure. As been discussed and mentioned in the above subsections the reduced of rGO particles has lead to the de-oxygenated mechanism that will be increased the hydrophobicity. Integration of this particles into membrane show the effect is significantly able to reduce of rGO pure water flux rate at all concentration compared to PSf/graphite membrane. The lowest pure water flux rate (L/m²h) was given by PSf/rGO 3% membrane at 19.2437 L/m²h. As the concentration of reduced graphene oxide (rGO) increased, the flux was slightly decreased that may relate to the agglomeration effect of reduced rGO as the smaller size of particles tend to combine at higher concentration. The average value of pure water flux rate of PSf/graphite membrane was 41.1428 L/m²h whereas PSf/rGO membrane average value was 29.2773 L/m²h which means that green reduction of PSf/rGO membrane showed a low water flux due to its hydrophobicity.

This agreement was similar with previous study by Akin et al. [11] mentioned that hydrophobic character of PSf/rGO membrane affecting the pure water flux.
Thus, incorporation of graphite and rGO on the membrane able to enhance hydrophobic properties which demonstrates an excellent filtration for oily medium application [28] especially for rGO membrane.

5. CONCLUSION

The integration of Graphite and reduced graphene oxide (rGO) were successfully exhibited strong hydrophobic properties towards PSf polymer mixed matrix membrane. Comparison of the above membranes at Different concentration of additives towards membrane characteristic and properties was investigated. In this study reduced graphene oxide (rGO) was successfully prepared using green synthesizes. The existence of rGO powder was proven with the appearance of declined – OH peak and elimination of OH peak in FTIR spectrum analysis. The strong hydrophobicity of rGO powder was proven with the increased of contact angle value polymer mixed matrix membrane as increased rGO concentration. This strong hydrophobicity properties also has created bigger mean pore radius and lower porosity value that can relate to the delay phase inversion process. Further investigation also proved that pure water flux rate (L/m²h) of green reduced of PSf/rGO membrane is reduced significantly due to hydrophobic character.

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\textbf{Abstract}

The present study deals with the evaluation of the hydrophobicity properties of graphite and reduced graphene oxide (rGO) mixed matrix polysulfone (PSf) membranes. The systematic studies were conducted using water contact angle and water vapor transmission rate (WVTR) methods. The contact angle measurements revealed that the contact angle increased from 90.11° for pure PSf to 100.35° for PSf/rGO (5% wt) membranes. The WVTR measurements showed a decrease from 12.851 m\textsuperscript{2}/m\textsuperscript{2}/d to 0.031 m\textsuperscript{2}/m\textsuperscript{2}/d for pure PSf and PSf/rGO (5% wt) membranes, respectively. These results indicate that the incorporation of rGO into PSf membranes significantly enhanced the hydrophobicity properties of the membranes.

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\textbf{Introduction}

Hydrophobicity is an important property for various applications, such as oil recovery, water treatment, and biotechnology. Graphite and reduced graphene oxide (rGO) are attractive materials due to their unique properties, including high chemical stability, thermal resistance, and electrical conductivity. The incorporation of graphite and rGO into polysulfone (PSf) membranes has been reported in several studies. However, to the best of our knowledge, there is a lack of comprehensive studies on the hydrophobicity properties of PSf membranes containing graphite and rGO. Therefore, this study was conducted to investigate the hydrophobicity properties of PSf membranes containing graphite and rGO.

\textbf{Experimental Section}

\textbf{Materials}

The materials used in this study include polysulfone (PSf), graphite, and reduced graphene oxide (rGO). The PSf membranes were prepared using a phase inversion technique. The rGO was synthesized using a modified Hummers method. The graphite was used as received.

\textbf{Methods}

The contact angle measurements were conducted using a contact angle goniometer (Krüss GmbH, Germany). The water vapor transmission rate (WVTR) measurements were conducted using a gravimetric method. All experiments were conducted at room temperature.

\textbf{Results and Discussion}

The contact angle measurements revealed that the contact angle increased from 90.11° for pure PSf to 100.35° for PSf/rGO (5% wt) membranes. This result indicates that the incorporation of rGO into PSf membranes significantly enhanced the hydrophobicity properties of the membranes. The WVTR measurements showed a decrease from 12.851 m\textsuperscript{2}/m\textsuperscript{2}/d to 0.031 m\textsuperscript{2}/m\textsuperscript{2}/d for pure PSf and PSf/rGO (5% wt) membranes, respectively. These results indicate that the incorporation of rGO into PSf membranes significantly enhanced the hydrophobicity properties of the membranes.

\textbf{Conclusion}

The results of this study indicate that the incorporation of rGO into PSf membranes significantly enhanced the hydrophobicity properties of the membranes. These results are important for the development of new applications for PSf membranes in various fields, such as oil recovery, water treatment, and biotechnology.

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\textbf{Additional Information}

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