Effect of Graphene Oxide (GO) on the Surface Morphology & Hydrophilicity of Polyethersulfone (PES)

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Abstract. Membrane has been widely used in water and wastewater treatment. One of the major issues related membrane separation is concentration polarization or fouling, which can lead to a decline of flux and premature failure of membrane. However, fouling can be controlled by modification of membrane properties such as morphology and hydrophilicity. In this work, a modification of polymeric membrane, polyethersulfone (PES) was carried out using graphene oxide in order to attain high antifouling characteristics. Graphene oxide (GO) was added at different compositions ranging from (0.1 wt%-1.0 wt%). GO was synthesized using modified Hummers' method and characterized using XRD and FTIR prior to using it as additive for the PES membrane. The prepared PES-GO composite membranes were characterized using FTIR and SEM, Contact angle measurement and pure water flux test were then conducted to investigate the hydrophilicity of the PES-GO membranes. It was found that the additions of GO has significantly improved the hydrophilicity of the membranes.

1. Introduction

An ideal membrane is a membrane that can produces a maximum permeate flux with the maximum solute rejection, reducing both capital and operating costs [1]. Membranes can be classified into two categories based on the materials, which are organic (polymeric) and inorganic (ceramic or metallic) [2]. According to Ahmad *et al*. [1], various polymeric membrane can be used in water and waste water treatments, such as cellulose acetate (CA), polysulfone (PS), polyethersulfone (PES), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), polyvinyl alcohol (PVA) and polyimide (PI). Among that, PES has been considered as the most significant polymeric membrane used for water application due to its transparent and amorphous properties, high transition glass temperature (Tg=225 ⁰C), high mechanical, thermal, and chemical resistances thus, ideal for asymmetric membranes with different pore sizes and surfaces [1]. However, there are some limitation of PES membranes owing to their hydrophobic surfaces, which boost the attachment of hydrophobic organic substances on the membrane surfaces or inside the membrane pores [1–4].

A few studies were performed in order to enhance the permeability and rejection rates and simultaneously reducing the fouling problems. Among the techniques proposed to improve the hydrophilicity and flux of the PES membranes were blending, grafting, chemical treatment, and coating. The blending/additives additions technique was considered as the best practice for surface improvement such as hydrophilicity, surface roughness, surface charge, and the pore size due to its convenient operation and mild conditions [1,5]. Graphene oxide (GO) is a 2D nanomaterials that has shown numerous advantages properties such as, high hydrophilic nature, promote negative surface charges, better miscibility with polymers, superior electron transport and high mechanical stability [4]. Ouyang *et al.*[6]*,* specified that GO contains extensive amount of covalently attached oxygen-containing groups, such as hydroxyl, epoxy groups, carbonyl, and carboxyl groups, which create

highly hydrophilic material. Lee et al. [7] prepared polysulfone/GO membrane for treatment of wastewater in membrane bioreactor. The membrane experienced higher resistance to both antifouling and anti-biofouling properties. The existence of GO in membrane material would encourage hydrophilicity which would certify high water permeation and obstruct biofouling due to the low interfacial energy between a surface and water. GO synthesized using Modified Hummers' method is better in compared to Brodie and Staudenmaier methods as it consists of fewer steps and the quality can be controlled easily [8].

2. Methodology

2. 1 Material
All chemicals used in the experiments were reagent grade. Graphite powders (Mw=12.01 g/mol, COMAK) were used as received. PES (Mw= 22,000 g/mol) and N, N Dimethylacetamide (DMAc) were purchased from Merck USA and used as polymer and solvent in preparation of cast solution. H_2SO_4 (98%, R&M Chemicals), $NaNO_3$ (84.99 g/mol, SYSTERM), $KMnO_4$ (158.05 g/mol, R&M Chemicals) and H_2O_2 (30%, Merck) were used as received. HCL and distilled water were used for washing method. Deionized water (DI) was used in sample preparation and for pure water flux (PWF) measurement.

2. 2 Graphene Oxide (GO) Synthesis
GO was prepared by using modified Hummer's method [9]. Preparation of GO consist of 6 stages, start with ice bath stage, stirring, stop reaction, washing, centrifuging and drying. In ice bath stage, 5 g of graphite powder, 2.5 g of sodium hydroxide, 200mL of concentrated sulphuric acid and 30 g of potassium permanganate were added into the beaker for 5 hours at temperature below 15 °C. Then, ice bath was removed and the mixture was stirred 20 hours at room temperature. Then, the mixture slowly heated to 70 °C for 2 hours and 90 °C for another 1 hour with addition of 100mL Distilled Water. Hydrogen peroxide was added to stop the reaction. The resulting mixture was continually washed by HCl dilution for several times. Followed by centrifuging and drying for 24 hours at 60-70 °C to form GO sheet.

2. 3 Fabrication of Composite Polyethersulfone – Graphene Oxide (PES-GO)Membranes
The PES-GO membranes were fabricated via phase inversion (immersion precipitation). The casting solution was prepared by using polyethersulfone (PES) and N,N-Dimethylacetamide (DMAc) as polymer and solvent, respectively. GO was used as a hydrophilic modifier/additive to improve the flux rate of membrane [10]. The addition of additives onto the PES membranes was carried out using blending technique forming composite PES-GO membranes. Different amounts of GO were added according to the Table 1 below and bare PES was prepared as a control experiment.

Table 1. Composition of additive and solvent to fabricate membrane for PES-GO Membrane.

Membrane	PES (wt%)	DMAc (wt%)	GO (wt%)
PES-0.1GO	17.0	82.9	0.1
PES-0.5GO	17.0	82.5	0.5
PES-1.0GO	17.0	82.0	1.0
Bare PES	17.0	83.0	0.0

GO was first dispersed in DMAc solvent and sonicated for 1 hour to obtain a homogenous casting solution. Then, PES was added slowly to GO/DMAc solution and stirred for 24 hours. PES was dried at 70 °C for 24 hours before used. Next, the prepared casting solution was cast onto the glass plate using glass rod, immediately immersed in distilled water coagulation bath for 24 hours to complete phase inversion process and dried under room conditions for another 24 hours.

2. 4 Characterization of GO and PES-GO membranes
X-Ray diffraction, XRD (Rigaku) analysis was first carried out to confirm the formation of graphene oxide from graphite. The measurement was performed in scanning range of 4 0 Kv, 40 mA, 5-80 °, (2

°/min). The distribution of GO in membrane and its functional group was observed using Fourier Transform Infrared (FTIR, Perkin Elmer). The spectra were recorded in the wave length range of 500-4000 cm^{-1}. The morphology of the membrane were then observed by using Scanning Electron Microscope, SEM (Hitachi, S-3400N).The hydrophilic behaviour of membranes was tested using water contact angle goniometer (AST Product INC, VCA-3000s). Pure water flux (PWF) test was then conducted to determine the permeation of water. The test was carried for at room temperature and 6 bar and finally, the flux was calculated by using equation (1) [10].

$$J = \frac{V}{A\Delta t} \tag{1}$$

Where J is pure water flux (L/m^{2}h), V is volume of permeate (L), A is effective area of membrane (m^2) and Δt is the sampling time (h).

3. Result &Discussion

3. 1 GO

Figure 1 compares the XRD spectra for graphite and GO in order to confirm the formation of GO from graphite. It was observed that the graphite has a very intense and sharp peak at $2\theta = 27.5^{\circ}$. After the oxidation and exfoliation process using modified Hummer's method, the sharp reflection of graphite was disappeared and a new peak was observed at $2\theta = 10.18°$. The disappearance of graphite peak of represents that graphite was altered after oxidation to completely formed graphene oxide. This is consistent with works by Tissera *et al*, [10] that the occurrence of oxygenated functional groups and interpolated water molecules in the graphite caused high interlayer space in the synthesized graphite oxide. It can be indicated that the graphite was fully oxidized due to no diffraction peak corresponding to graphite at XRD spectrum of synthesized graphene oxide.
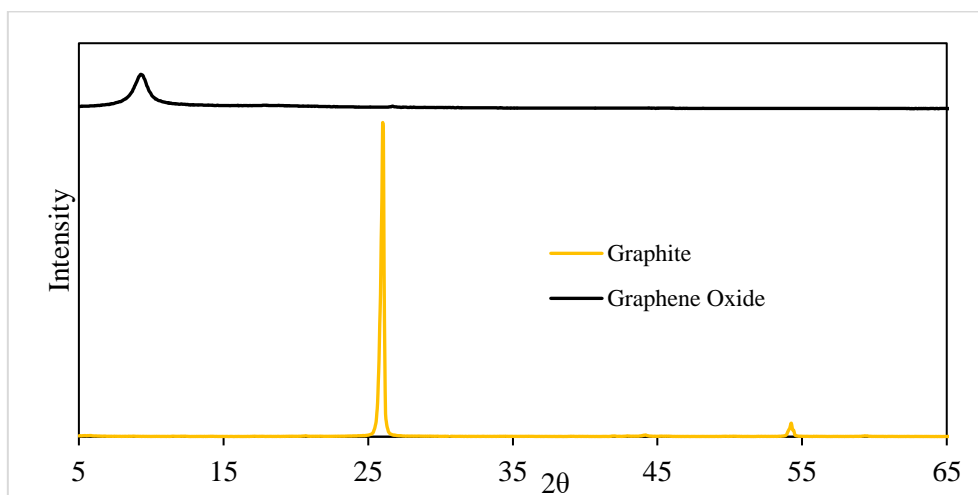

Figure 1. XRD pattern for Graphite and Graphene Oxide.

3.2 *Properties of Composite PES-GO Membranes*

Figure 2 shows the FTIR spectra for bare GO, PES membrane and composites PES-GO membranes. This analysis was conducted to observe the compositions and to identify the functional groups of membranes upon the introduction of GO. From Figure 2, it can be confirmed that GO is a hydrophilic material with a number of functional groups such as hydroxyl (O-H = 3500cm^{-1}), carbonyl (C-C) similar with worked done by Yu *et al* [11]. After the introduction of GO, this spectrum indicates the GO was entrapped and formed as one part of PES structure which responsible for enhancing the hydrophilic characteristics of the membrane. There are large amounts of oxygen-containing functional groups, including carboxyl, hydroxyl, and carbonyl, on GO is due to oxidation which responsible for hydrophilic characteristics of GO.
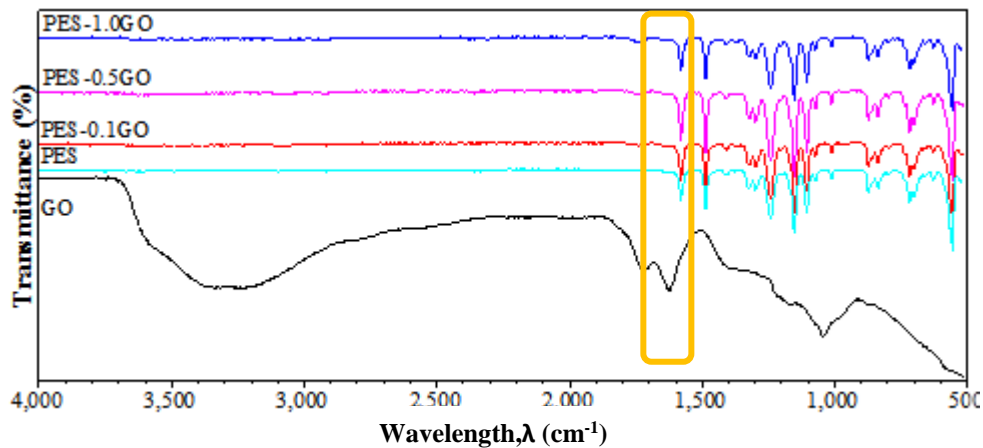
Figure 2. FT-IR of GO, PES, PES-0.1GO, PES-0.5GO and PES-1.0GO.

3.3 Hydrophilicity properties of the composite PES-GO membranes
Figure 3 displays the contact angle and pure water flux values for the composite PES-GO membrane. Lower water contact angle indicates that the membranes are more hydrophilic. From the contact angle plot, it can be seen that the contact angle decreased from 59° to 46° when 1.0 wt% of GO was added into the PES membrane. This value is significantly low in compared to Jin *et al* [12], which the contact angle was 78° to 55°. The pure water flux was also observed to increase with the amount of GO achieving 123 L/m^{2}h. This value was significantly higher in compared to other results in Safarpour *et al.* [5], where Titanium Oxide was used. The high increment of PWF might be due to the highly hydrophilic properties of GO.
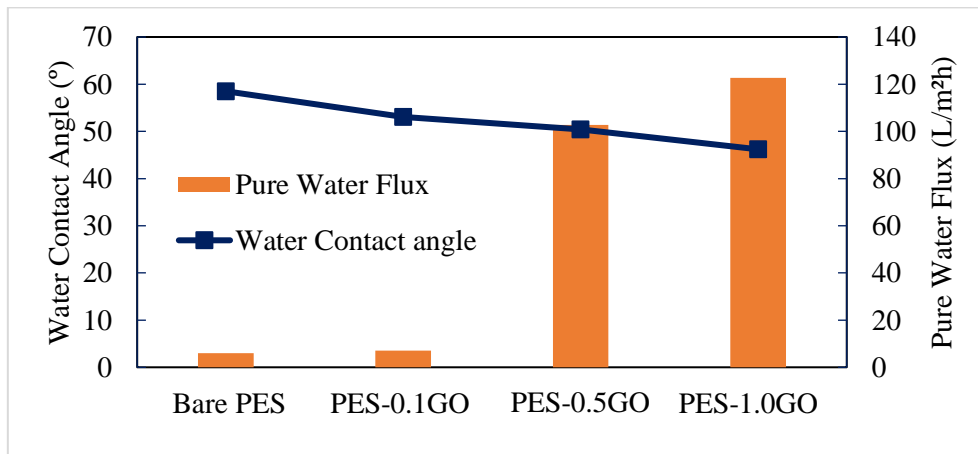

Figure 3. Pure water flux test water contact angle of composite PES-GO membranes.

Figure 4 shows the stability of pure water flux for 1 hour. The result shows that the pure water flux was in a stable mode for all the membranes. This indicates that the membranes are stable with time. A stable membrane is required due to highly hydrophilic which has lower contact angle value and produced high water permeate [12].
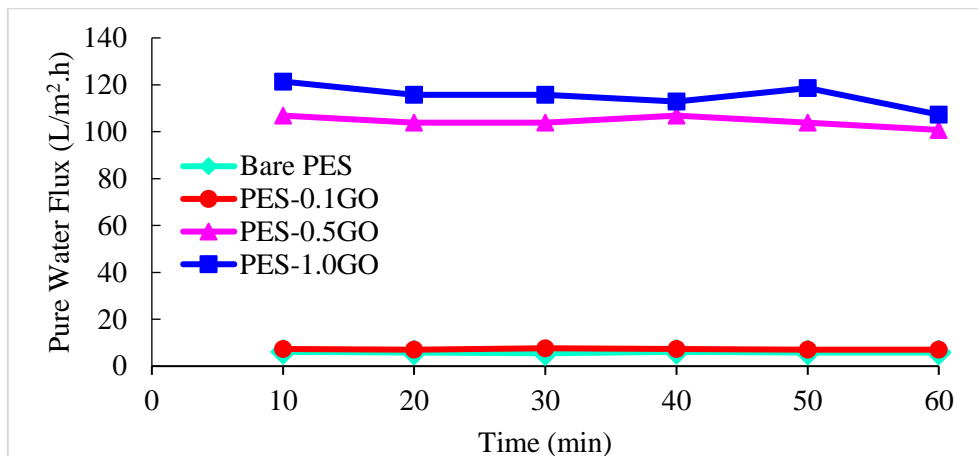
Figure 4. Pure water flux stability.

3.4 Morphology of Composite PES Membranes

Figures below represents the cross-sectional image of Bare PES membrane, PES-0.1GO, PES-0.5GO and PES-1.0GO respectively. Hydrophilic additives can be used to improve the pure water flux of the membrane and at the same time minimizing the fouling issues [4]. From the PWF and contact angle studies, it was observed that the addition of GO can significantly affected the hydrophilicity of the PES membrane due to present of hydroxyl and carbonyl functional group in GO. The morphology of the bare PES membranes shows the interactions of polymer and solvent and hence produced more porous membrane. As a result, the size of fingerlike structure amplified. It is seen that with the addition of GO, the surface roughness on the membrane surface increases progressively causing in the formation of numerous pores [12].
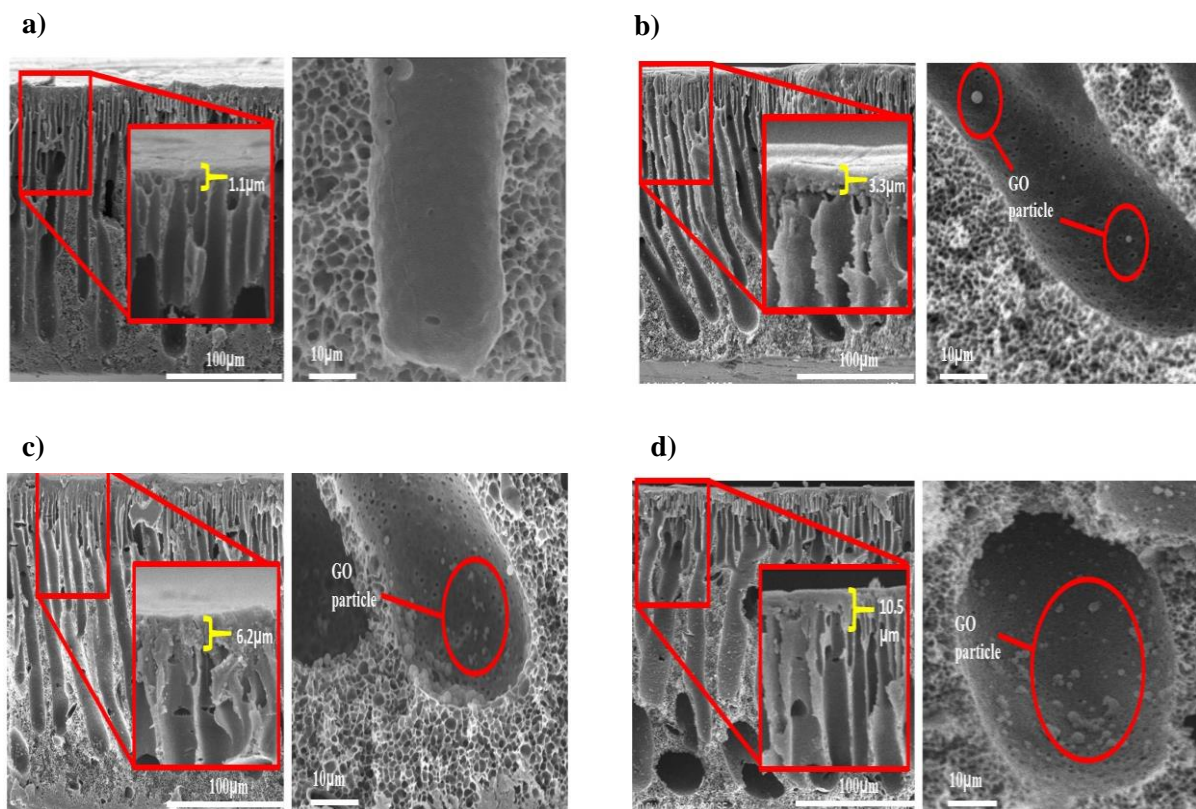

Figure 5. SEM images of a) bare PES membrane, b) PES-0.1GO, c) PES-0.5GO, and d) PES-1.0GO

Figure 5 indicated that as more GO added, the finger-like structure bend slightly and the bottom part become bigger. This is due to high hydrophilicity of GO that attract more water during phase inversion. The thickness of membrane skin layer also increase with addition of GO. The presence of more GO particle can be spotted as more GO added. Razaee *et al*. [4] mentioned that the faster the exchange rate of solvent and non-solvent in the coagulation process, the larger pores, more finger like pores and more channels.

4. Conclusion

Graphene oxide was successfully synthesized using modified Hummer's method and used as additives for the modification of PES membranes. Based on the contact angle and pure water flux test, it was found that the composite PES-1.0GO membrane exhibited the most hydrophilic characteristic due to the high amount of GO. From the SEM image, it can be seen that GO was homogeneously dispersed in the PES membrane. Based on the result obtained, it is strongly believed that GO can serve as a highly hydrophilic modifier for PES membrane fabrication, thus minimizing the fouling problems.

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