Penerbit Akademia Baru

Journal of Advanced Research in Materials Science

Journal homepage: www.akademiabaru.com/arms.html
ISSN: 2289-7992

Advanced Research in Materials Science

Preparation and Characterization of Polyethersulfone/Natural Clay Nanocomposite Membrane

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ARTICLE INFO

Article history:
Received 5 July 2018
Received in revised form 14 October 2018
Accepted 2 December 2018
Available online 15 March 2019

ABSTRACT

Polyethersulfone (PES) is hydrophobic polymer that is prone to membrane fouling which lead to low water flux and the adsorption of foulants onto membrane surface. Therefore, the addition of natural clay into polyethersulfone/natural clay (PES/NC) nanocomposite membrane can be a way to improve the properties of PES original membrane to overcome membrane fouling. The objectives of this study were to characterize PES and PES/NC nanocomposite ultrafiltration membrane in terms of its morphology, water content, porosity, and pure water permeation as well as permeability coefficient of PES and PES/NC membrane. Scanning electronic microscope (SEM) results revealed that more finger-like pores on asymmetric PES/NC nanocomposite membrane compare to PES native membrane. The water content and porosity were increased as amount of natural clay increased. Besides, performance of membrane was tested by using pure water permeability (PWP). The results revealed that the PWP was directly proportional to the applied pressure. The data from PWP also indicated that the increment of permeability coefficient from 11.831 L/m².hr.bar to 15.286 L/m².hr.bar with the increment clay composition from 0.4 to 0.8 wt%. These results revealed that the incorporation of natural clay into PES membrane had enhanced its hydrophilicity properties and proved these PES/NC nanocomposite membrane has anti-fouling membrane properties.

Keywords:
Polyethersulfone, natural clay, nanocomposite, membrane, fouling

1. Introduction

Membrane filtration is becoming more popular as a green technology and this technology has been largely used in different applications such as food industry, water treatment, pharmaceuticals, and biochemical engineering [1]. The primary advantage of this technology in water treatment technology is it is simple filtration process with no chemical addition as well as low energy usage and easy process. This technology also has been used to remove unwanted compounds and pathogens which produced a good water quality and taste [2].

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The most of commercial synthetic membranes in separation industry are based on polymeric materials such as polysulfone (PSf), polyethersulfone (PES), polyvinylidiene fluoride (PVDF) and polypropylene (PP). These polymer based membrane are attractive choice in wastewater treatment and drinking water production due its potential to remove assorted contaminants.

They have being employed in many industries, however, is in the limited range of application due to the occurrence of fouling [3]. Membrane fouling is typically caused by inorganic and organic materials presented in water that adhere the surface and pores of membrane [1]. This fouling cause the decrease in permeation flux which frequent cleaning is required to cope with this problem and leads to increase in energy demands and reduce membrane lifespan [4].

The addition of inorganic particles to polymer membrane become an attractive method for synthesis of new polymeric membrane in order to reduce membrane fouling problem. Polymer clay nanocomposite membrane is considered as one of the latest composite type. For this kinds of composite, polymer acts as a matrix whereas the reinforcement material is clay mineral. The combination of two structures can aid in the synthesis of new materials which have better chemical and physical properties according to their components [5]. The application polymer clay nanocomposite is a promising option to develop antifouling membranes [6]. Hence, in this study natural clay from local source was employed in PES nanocomposite membrane in order to study their improvement of the original membrane in terms of morphological structure, water content, porosity, permeability, hydrophilicity, and pure water flux.

2.Materials

All materials used were analytical grade. The membrane were fabricated from the dope solution of polyethersulfone (PES) as the base polymer and N-methyl-2-pyrrolidone (NMP) as a solvent. The natural clay was obtained from Kampung Dengir, Besut, Terengganu. Distilled water was also used throughout the experiments.

3.Methodology

3.1 Membrane Preparation

The membrane were prepared via phase inversion method as described by Ali *et al*., [7]. Different natural clay content (0.4 and 0.8 wt%) were added into a 17/83 wt% of polymer/solvent solution and homogenous dispersion solutions were prepared by mechanical stirring for 6 h at 70 ^{o}C. Membrane were fabricated via phase inversion technique and the membrane were stored in distilled water for prior usage. The original membrane was marked as PES (without clay content) and two other nanocomposite membrane were named as PES/NC-4 and PES/NC-8 for the natural clay composition of 0.4 and 0.8 wt% respectively.

3.2 Membrane Morphology

The Scanning Electron Microscopy (SEM) (JSM P/N HP475 model) at Institute of Oceanography, Universiti Malaysia Terengganu (UMT) was used to analyse morphological structure of PES and PES/CN nanocomposite membrane. SEM was used to inspect the cross-section of the fabricated membranes. The membrane samples were fractured in liquid nitrogen and sputtered with gold, before transfer and analysed by using the microscope.

3.3 Water Content

The membrane was soaked in water for 24hours and mopping with blotting paper to obtain the water content by weighing them. Next, the wet membranes were placed in vacuum drier at 75^{o}C for two days (48h). After the membranes were dried, the dry weight will determine. Equation (1) below was used to calculate the percent of water content [8].

$$\text{water content } \% = \frac{(Wwet - Wdry)}{Wwet} \times 100 \tag{1}$$

$Wwet$ = wet sample weight
$Wdry$ = dry sample weight

3.4 Porosity

The method of dry-wet weight was used to measure the porosity of membrane. The membrane samples were soaked and weighed. After that, the wet membrane were dried in desiccator for 48 hours. The dry weight of membrane samples was weighed by using an analytical balance. Porosity of the membrane samples was calculated by using Equation (2) as shown below.

$$\text{Porosity } = \frac{(Ww - Wd)}{pw \times A \times \delta} \tag{2}$$

Ww = wet sample weight (g)
Wd= dry sample weight (g)
pw = density of pure water (g/cm^3)
A = area of membrane in wet state (cm^3)
δ = thickness of membrane in wet state (cm)

3.5 Pure Water Permeation (PWP) Test

The experiment of PWP was conducted by a dead-end cell system with the processing volume of 300 ml distilled water was used in this test. Before conducting the permeation test, membranes was compact for 30 minutes and permeate was collected for every 2 ml until a steady state was attained. After the compaction process, PWP test was carried out at different system pressure in the range of 1 to 5 bars. Then, permeate was collected and the pure water permeation (PWP) was calculated by using Equation (3) below [8].

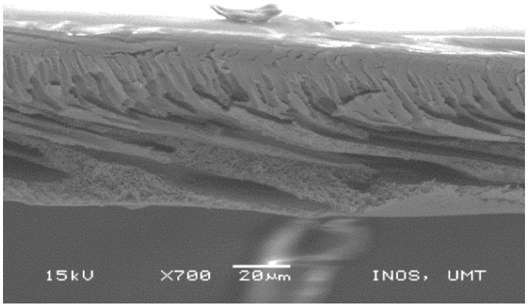
$$\text{PWP} = \frac{Q}{\triangle t \times A} \tag{3}$$

PWP = pure water permeation (Lm^{-2} h^{-1})
Q= amount of permeates collected (L)
$\triangle t$ = sampling time (h)
A = membrane area (m^2)

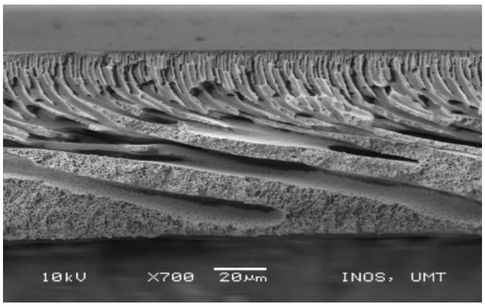
4.Results and Discussion

4.1 Membrane Morphology

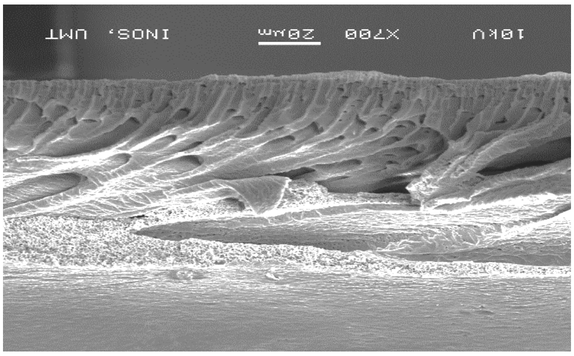
Figure 1 depicted cross-sectional SEM micrograph of morphological structure of PES membrane. All the fabricated membranes shown as asymmetric membrane structure. The membranes consisted of two layers which are active layer and supporting layer. Both layer provided important roles in membrane transport property. Skin of active layer control the selectivity and separation process whereas the support layer lies below acts as a supporting structure. The porosity of the supporting structure is generally much greater as compared to the top layer [9]. It can be clearly seen that the morphology of membranes changed with the addition of natural clay in PES/NC composite membranes.



(a)



(b)



(c)

Fig. 1. SEM Micrograph of Cross Sectional View of PES and PES/NC Nanocomposite Membranes; (a) PES ; (b) PES/NC-4; (c) PES/NC-8

It can be observed that the corresponding membrane have skin active layers which comprises the finger-like structures and the formation of macrovoid structure at bottom layer. Figure 1 (a) illustrated that the virgin PES membrane has long and narrow finger-like structure. It extends from top to the bottom with a slight open channel. The sub-layer of PES membrane shows the existence of dense spongy structure due to hydrophobic properties of PES polymer in membrane dope solution. Ali *et al*., [10] has explained that the spongy structure formed beneath the skin layer due to delayed phase separation occurred during phase inversion process. Polymer with hydrophobic properties promotes delayed phase separation during membrane fabrication process.

Incorporation of natural clay in PES membrane has effect a drastic changed in membrane morphology as shown in Figure 1 (b) and 1(c). When the concentration of natural clay increased, the microvoid walls became more porous and Anadão *et al*. [11] had observed the same results in their study. Moreover, the membrane were noticed to increase in the number of finger-like pores as the content of natural clay increased. The appearance of macrovoids in PES/NC-8 proved that the presence of high amount natural clay enhanced the phase inversion of liquid-liquid demixing process during membrane fabrication. This phenomenon is known as an instantaneous liquid-liquid demixing process [10].

4.2 Water Content and Porosity

The percentage of water content and porosity was calculated using Equation (1) and Equation (2), respectively. All the results obtained for native PES membranes and PES/NC composite membrane were tabulated in Table 1. As shown in Table 1, PES has the lowest water content and porosity, 60.84 % of water content and 1.008 of porosity. When the membranes were added with the natural clay from 0.4 wt% to 0.8 wt%, the value of water content were increased to 61.53 wt% and 62.15% for PES/NC-4 and PES/NC-8, respectively. Increased the composition of natural clay in PES membrane also improved the porosity of membrane structure from 1.008 to 1.088.

Table 1
Water Content and Porosity of Native PES Membrane and PES/NC Nanocomposite Membrane

Membrane	Water Content(%)	Porosity
PES	60.84	1.008
PES/NC-4	61.53	1.055
PES/NC-8	62.15	1.088

The increment in water content because of the detachment of polymer chains from the silica surface which led to interface voids. Furthermore, this causes an increase in void volume resulting in the formation of bigger size pores on the membrane surface and increases the water uptake in the pores The incorporation of natural clay to the membrane dope improved the inflow rate of water and accelerated the exchange process between the solvent in polymer dope and non-solvent in coagulation bath and consequently increased the ratio of water content and porosity of fabricated membranes [7].

Hydrophilicity of membrane is related to the water content of membrane [8]. Hydrophilicity and porosity are two important parameters for membrane in the separation process and membrane permeation. They also have close relationship with the morphology and pure water permeation of membranes [6]. Based on the results in Table 1, it was revealed that the increment of natural clay in PES/NC nanocomposite membrane had enhanced its water content and porosity in consequence also increase their hydrophilicity properties of PES membrane.

4.3 Pure Water Permeation (PWP) Test

PWP test was employed to measure the permeability of native PES membranes and PES/NC nanocomposite membrane at different pressure. Each piece of the fabricated membrane was tested at least three times to ensure the consistency of results obtained. Figure 2 shows the graph of pure water permeation versus pressure for different composition of PES/NC composite membrane.

From the figure, it can be observed that all the membrane possessed the linear line profile. This revealed that the PWP is directly proportional to the applied pressure. All the fabricated membranes had lowest flux at the lowest applied pressure which was at 1 bar. When the applied pressure was increased from 1 to 5 bar, the PWP of membrane shown gradually increment trend. Besides that, increased composition of natural clay in PES membrane will increase PWP of the composite membrane. It was due to hydrophlicity properties of the composite membrane also increased. The slopes of the graphs indicating the permeability coefficient of each PES/NC composite membranes and it was tabulated in Table 2.

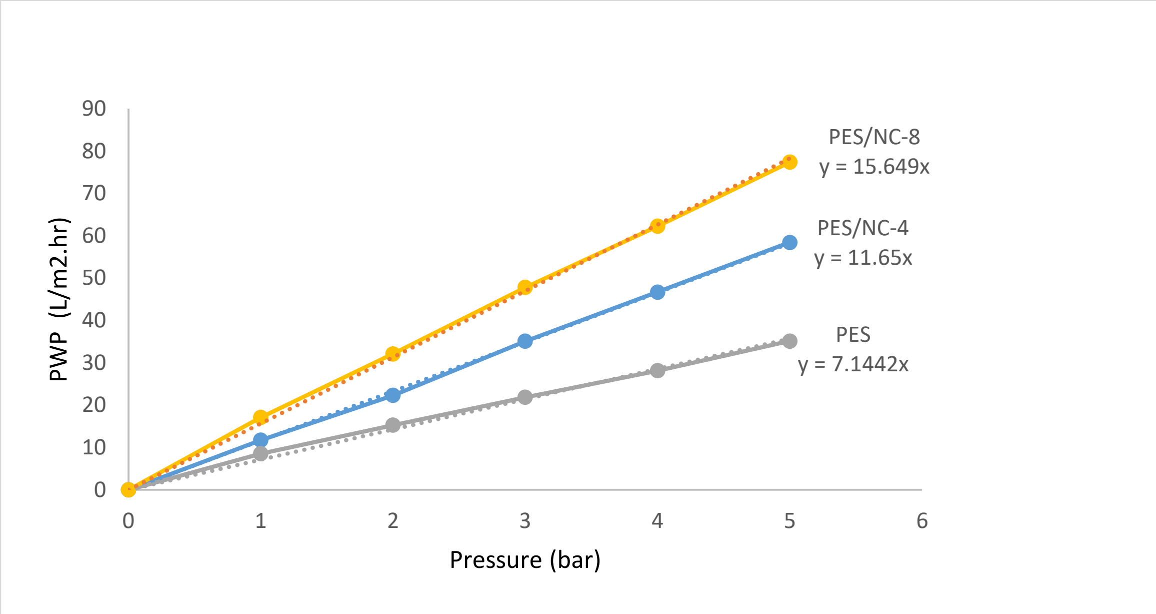


Fig. 2. Pure Water Permeation of PES and PES/NC Nanocomposite Membrane at Different Operating Pressure

The membrane permeability coefficient is an intrinsic property of membrane which is indirectly used as an indicator to its hydraulic resistance and porosity of ultrafiltration membranes. As shown in Table 2, all the membranes exhibited increment in permeability coefficient as the composition of natural clay increased. The permeability coefficient for PES was 7.189 L/m².hr.bar. Then, when the composition of the natural clay was increase in PES/NC 17-4 and PES/NC 17-8, it shows the increment of permeability coefficient to become 11.831 L/m².hr.bar and 15.286 L/m².hr.bar, respectively.

Table 2
Permeability Coefficient of Native PES Membrane and PES/NC Nanocomposite Membrane

Membrane	Permeability Coefficient(L/m^2.h.bar)
PES	7.189
PES/NC-4	11.831
PES/NC-8	15.286

According to Rejabi *et al.*, [13], the incorporation of hydrophilic clay into the casting solution enhances the water affinity of polymeric casted films towards water compared to native PVDF membrane resulting in increasing of the penetration velocity of water into the fabricated membrane. Moreover, the increment of water permeation is attributed to the asymmetric and opened structure of membrane as well as improve of membrane's hydrophilicity and porosity when clay was added [14]. Membranes with predominantly larger diameter and unhindered finger-like internal pore structure are most appropriate for achieving high water permeability during water or wastewater treatment [15].

5. Conclusion

SEM micrographs shown PES membrane has tight and tiny finger-likes structure and spongy support layer due to its hydrophobic properties. While PES/NC nanocomposite membrane which contained natural clay illustrated open finger-likes structure with more microvoids and macrovoids presence at the support layer of the membrane. The water content and porosity were increased by increasing natural clay composition. When the membrane were added with the natural clay from 0.4 wt% to 0.8 wt%, the value of water content and porosity were increased to 61.53 wt% and 62.15 wt%, and 1.055 and 1.088 for PES/NC-4 and PES/NC-8, respectively. The PWP and permeability coefficient of PES/NC nanocomposite membrane also increased with the increment of natural clay content. PES/NC-8 membrane shown the highest PWP and permeability coefficient compare to PES and PES/NC-4 membrane. These results proved that the addition of natural clay has improved the hydrophilicity properties of PES membrane which in turn enhanced its anti-fouling properties.

Acknowledgements
The authors would like to acknowledge the financial support from School of Ocean Engineering, Universiti Malaysia Terengganu for the Allocation of Final Year Research Project in this research.

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