

# Influence of Multiwall Carbon Nanotube on Polyethersulfone/ Polyvinyl Alcohol Blend Membranes

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## Article history

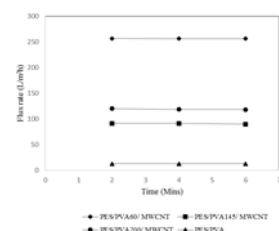
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## Graphical abstract



## Abstract

This paper investigates the influence of multiwall carbon nanotube (MWCNT) on the morphology and properties of polyethersulfone (PES) and polyvinyl alcohol (PVA) blend membranes. Several membranes were prepared by blending 0.5 wt% MWCNT, 18%wt PES and 1.5wt% PVA of various molecular weights (60, 145 and 200 kDa) in dimethyl acetate (DMAC) solvent. The membranes were then evaluated in terms of its morphology, contact angle, water flux rate and porosity. The results revealed that MWCNT nanoparticles have decreased the contact angle and increased the flux rate of PES/PVA blend membranes. The presence of MWCNT in the PES/PVA membranes have promoted the formation of fingerlike pores in the membranes structure and thus increased the porosity of the membranes. Besides that, the use of higher molecular weight PVA helped to reduce the contact angle of the membranes reflecting to their hydrophilic nature. However, the use of lower molecular weight PVA was found to enhance the increased of flux rate and porosity of the membrane.

**Keywords:** Multiwall carbon nanotube; polyethersulfone; polyvinyl alcohol; blend membrane; ultrafiltration membrane

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## 1.0 INTRODUCTION

Polyvinyl alcohol (PVA) has been used in polyethersulfone (PES) membrane preparation mostly as composite layers. Most of previous work involved the fabrication of microporous PES membranes by phase inversion followed by coating with 5 wt% of PVA and 0.5 wt% of crosslinking agent (maleic acid). Such PES membranes were used to separate ethanol from water mixtures by pervaporation process and result achieved shows that the separation factor increase with the increasing number of coating steps of PVA solution at the expense of total flux [1]. In another study, the prepared PES membranes were dip-coated twice into PVA solution so as to ensure that the PES membranes were fully covered by PVA solution thus minimizing morphological defects. The obtained results indicates that the prepared membrane exhibited high separation factor as well as high permeation flux [2]. The presence of PVA coating on PES membrane have led to a remarkable reduction in contact angle, increment in the wettability and adhesion of PES surface due to its hydrophilic nature.

Recently, nanoparticle materials were also used in PES/PVA membranes. Basically nanoparticles were employed in PES

membrane to improve hydrophilicity of the membrane. Previous research studied the effect of titanium oxide nanoparticles (TiO<sub>2</sub>) on PES/PVA membrane [3]. The PES polymer was coated with PVA and TiO<sub>2</sub> solution separately. The results revealed that the membrane has lower degree of swelling, perform better in terms of flux and salt rejection rate. The formation of polar groups on the membrane surface due to the presence of TiO<sub>2</sub> allows interaction with water molecules through van der Waals' force and hydrogen bonds. Thus, the permeation rate of water through the composite PES coated with TiO<sub>2</sub> and PVA membranes was high.

Among nanoparticles that available, MWCNT has become attractive because it is easy to modify and have extraordinary electrical and mechanical properties. MWCNT has a strong tendency to agglomerate due to their nanosize and their respective high surface energy. Therefore modification of MWCNT by chemical functionalities such as carboxylates, render MWCNT to have negative charges and creates the electrostatic stability for a colloidal dispersion [4].

Thus, it is interesting to study the influence of MWCNT as the additive in PES/PVA blend membrane and to observe the reaction between carboxyl groups of MWCNT with hydrophilic PVA.

Furthermore, the effect of mixing PVA as an additive in PES polymer solution with MWCNT via blending method for water separation has not been reported yet. Different molecular weights PVA were used in the experiment to analyze the effect of the molecular weight towards membrane performance. The addition of MWCNT into PES polymer and the use of PVA polymers were expected to improve membrane performance due to the presence of hydroxyl and carboxyl groups. Both groups from PVA and MWCNT could contribute to hydrogen bonding in PES membrane structure. Such partially positive charged hydrogen in PVA polymer structure atom may have weak interaction with the oxygen atom and thus form hydrogen bonds that increase hydrophilicity.

## 2.0 EXPERIMENTAL

### 2.1 Membrane Materials

Polyethersulfone polymer was purchased from BASF and dried in an oven at 70°C overnight so as to remove any moisture available. Carboxylic functionalized acid treated multiwall carbon nanotubes (MWCNT) (Average diameter; 11 nm, Length; 15 µm) were purchased from local supplier. Dimethylacetamide (DMAC) as a solvent and polyvinyl alcohol, fully hydrolysed with different range of molecular weight (60, 145 and 200 kDa) were purchased from Merck.

### 2.2 Membrane Fabrication

Membrane solution was prepared by blending PES, MWCNT and PVA to form a dope solution. The dope solution was prepared by dissolving 1.5 wt% of PVA and 0.5 wt% of functionalized MWCNT in DMAC solvent at 80°C. The homogenous dope solution was then held at ambient temperature for a while to remove any air bubbles present. 18 wt% of PES was then added to the dope solution and dissolved homogeneously at high temperature using a hot plate. The resultant dope solution was then allowed to cool and ultrasonicated so as to remove air bubbles. The dope solution was then casted on a glass plate using a casting knife and the glass plate was immediately immersed into distilled water to form a thin membrane flat sheet of approximately 200 µm in thickness. The flat sheet membranes were then washed with distilled water and stored in distilled water until use.

### 2.3 Membrane Characterization

#### 2.3.1 Membrane Morphology

The PES/MWCNT/PVA membrane surface and morphology were analysed using field emission scanning electron microscopy (FESEM). The flat sheet membrane was first cut into pieces and immersed in liquid nitrogen to obtain a clean cut cross section of the membrane sample.

#### 2.3.2 Contact Angle

The surface hydrophilicity of the membranes was determined by contact angle measurement. Low value of contact angle shows that the membrane is hydrophilic. The contact angle measurement was performed using dynamic sessile drop. 2 µL of distilled water was dropped onto a dry membrane surface using a micro-syringe, and the contact angle was measured. At least five readings of contact angles were taken to obtain average value.

#### 2.3.3 Water Flux Rate

The water permeability of the membrane was examined by passing water in a cross-flow cell as shown in Figure 1. The operating pressure was at 1 bar and the membrane effective area is 33.15 cm<sup>2</sup>. The permeation flux was calculated using the following equation:

$$J_w = \frac{V}{A\Delta t} \quad (1)$$

where, V is the volume of permeated water (l), A the membrane area (m<sup>2</sup>), and Δt the permeation time (h).

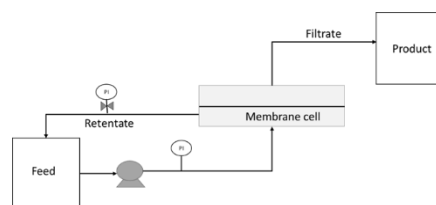


Figure 1 Cross flow filtration diagram

#### 2.3.4 Porosity

The porosity (ε) of the membrane was determined using dry-wet method and was calculated using the following equation:

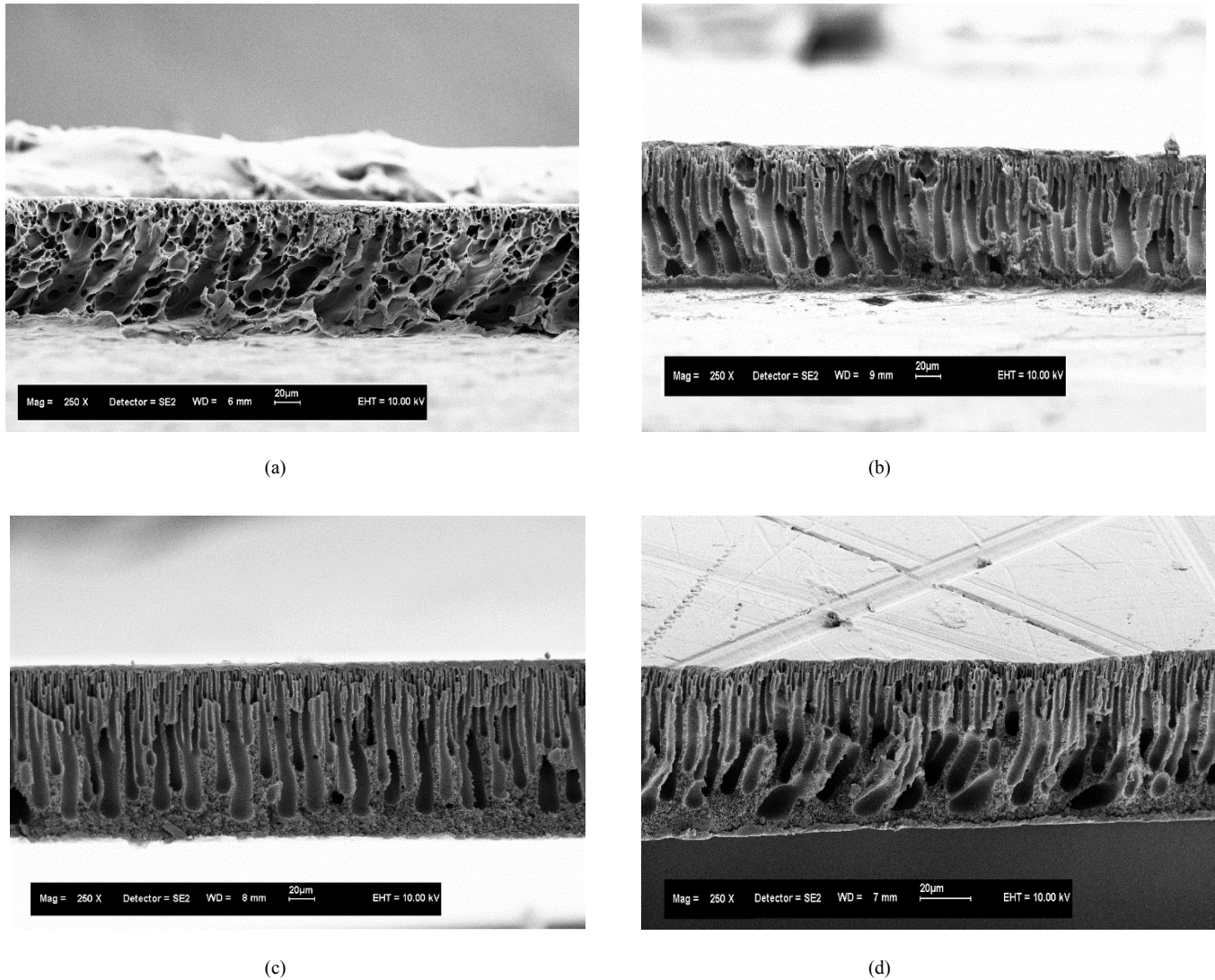
$$\varepsilon = \frac{w_1 - w_2}{A \times l \times d_w} \quad (2)$$

where w<sub>1</sub> is the weight of wet membrane (g), w<sub>2</sub> is the weight of dry membrane (g), l is the membrane thickness (cm) and d<sub>w</sub> is the water density (0.998 g/cm<sup>3</sup>).

## 3.0 RESULTS AND DISCUSSION

### 3.1 Morphology of Membranes

FESEM observation of membranes cross sections revealed that PES/PVA membranes with MWCNT produced long pore like finger structures as shown in Figure 2 (b-d). The structures were vertically interconnected and almost did not have any horizontal blockage compared to PES/PVA membrane without MWCNT. As illustrated in Figure 2 (a), membrane without MWCNT contained many small pores. Thus, this indicates that functionalized MWCNT additive is responsible for the formation of the structure of the pore like finger which is important for membrane permeability. Functionalized carbon nanotubes is believed to have created strong bonds with PVA via hydrogen or covalent linkages. This hypothesis is supported by the findings of previous researchers which indicated that the mixing of carbon nanotubes and PVA makes the local glass transition (T<sub>g</sub>) temperature of the polymer to shift to higher temperature [5]. Moreover, the length of acid-functionalized carbon nanotube is often shortened during functionalization<sup>4</sup> and thus they could uniformly interact with the polymer matrix. The yield of carboxyl and hydroxyl functional group from MWCNT and PVA in the membrane solution have also help the formation of fingerlike pore structures in the membrane sub-layer. It is believed that the fast exchange between solvent and non-solvent in the phase inversion process occurred due to the addition of both hydrophilic substances and thus creates the porous structure as depicted in the FESEM images [6].

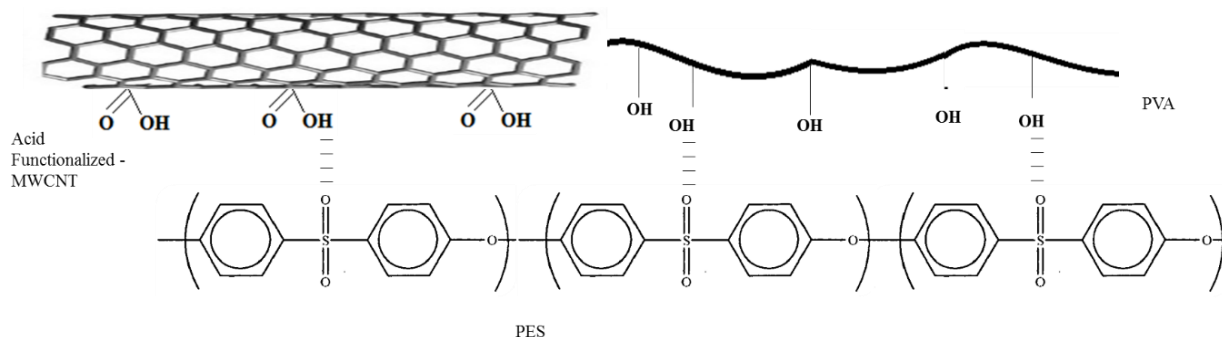


**Figure 2** FESEM cross-sectional images of the (a) PES/60 kDa PVA without MWCNT: (b) PES/60 kDa PVA/MWCNT, (c) PES/145 kDa PVA/MWCNT, (d) PES/200 kDa PVA/MWCNT

### 3.2 Contact Angle

Blending the carbon nanotube particles with PES material has increased hydrophilicity in membrane surface as reported in previous research due to the hydrogen bonding interaction of carbon nanotubes with sulfonic group of PES material [7] PVA material which is rich in  $-OH$  bonds was also believed to effectively enhance the surface hydrophilicity of PES membrane [8]. Therefore, PES/PVA/MWCNT membrane demonstrated low contact angle as shown in Table 1. The results also revealed that hydrophilicity of the membranes were affected by PVA molecular weight. Higher molecular weight PVA gave lower value of contact angle which means increase in hydrophilicity. This could probably be due to the PVA molecules which entangled together and lead to frequent hydrogen bonding reactions with PES and MWCNT as illustrated in Figure 3. This findings were also similar with a research where increase in concentration of chitosan polymer have

increased intermolecular reaction within the chitosan molecules and PES, increased hydrogen bonding reactions and thus increased the polymer hydrophilicity [9]. High contact angle was achieved for PES/PVA membrane due to the absence of MWCNT that contribute to hydrogen bonding in membrane structure.



**Figure 3** The structure of hydrogen bonding between the sulfonic group of PES and carboxylic group of acid functionalized MWCNT and hydroxyl group of PVA

**Table 1** Result of contact angle measurement for the membranes

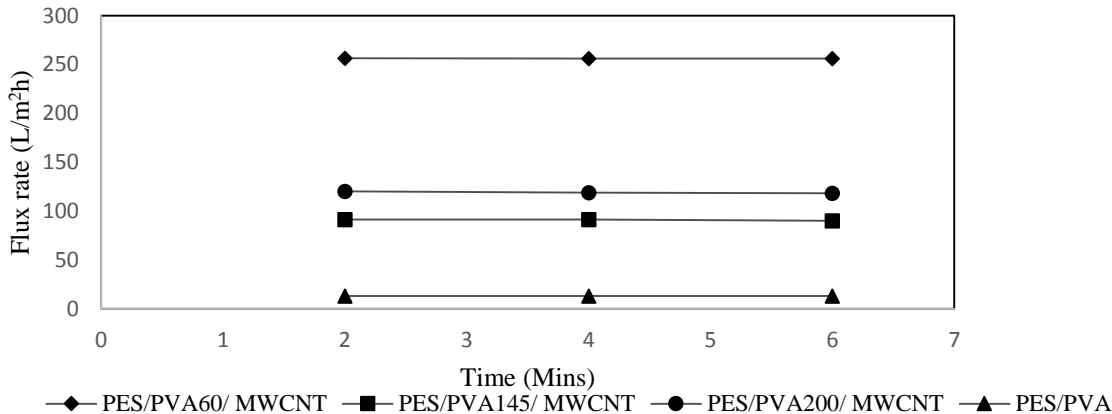
Membrane	Contact angle (°)
PES/PVA	74.00
PES/PVA (60 kDa)/ MWCNT	71.48
PES/PVA (145 kDa)/ MWCNT	69.82
PES/PVA (200 kDa)/ MWCNT	64.90

### 3.3 Flux Rate and Porosity

In previous study of TiO<sub>2</sub> with PES/PVA membrane, the results for water flux were at 40-45 L/m<sup>2</sup>h<sup>3</sup> and maximum water flux achieved by other PES/MWCNT membrane research was at 93 L/m<sup>2</sup>h [10]. However in this study, the water flux for all the blend membranes were higher (Figure 4) compared to the previous study. The water flux graph shown in Figure 4 indicates that highest water flux rates

was achieved by lower molecular weight PVA membrane. It is believed that besides the factor of membrane structure factor, orientation of PVA molecule in the PES membranes would have also effect the water flux of the membrane.

Increased of PVA molecular weight result in decreased in free volume as the length of polymer chains in the membrane increased and the chain being more entangled and hindered water permeation [11]. However, increased of PVA molecular weight might also associated with the increasing degree of disorder of amorphous region and lead to the increase of free volume that promote higher water vapor permeation of the membrane [12]. Thus, this probably the reason of membrane with higher molecular weight PVA (200 kDa) also obtained slightly increased in flux. Furthermore, as shown in Figure 4 lowest water flux was achieved by PES/PVA membrane without MWCNT. This was confirmed by the presence of small micropores in the membrane's sub layer structure as depicted in the FESEM image (Figure 2a).



**Figure 4** Membrane flux rate of PES/MWCNT/PVA membranes

Moreover, the porosity of the membrane results in Table 2 shows an agreement to the water flux achieved in the study. High porosity is related to the long microvoids (finger-like structure) of membrane structure. As the vacancies volume into the membrane structure increased, the absorbed amount should be higher due to many free paths for fluid to flow.

**Table 2** Result of the membranes porosity

Membrane	Porosity, $\epsilon$
PES/PVA	0.52
PES/PVA (60 kDa)/ MWCNT	0.95
PES/PVA (145 kDa)/ MWCNT	0.69
PES/PVA (200 kDa)/ MWCNT	0.85

### 4.0 CONCLUSION

The addition of MWCNT in PES/PVA solution has a significant influence on membrane morphology, contact angle and permeation rate. Finger-like structures were achieved in PES/PVA with the MWCNT and such structures promotes higher water flux rates. It can be conclude that the water flux rate and porosity was increased when the molecular weight of PVA decreased. Moreover, membrane hydrophilicity increased with addition of MWCNT and higher molecular weight of PVA due to probability of the increase in hydrogen interaction from both additives with PES polymer chain. The future for PES/PVA/MWCNT membrane looks promising due to the excellent flux rates achieved.

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