RESEARCH ARTICLE

Polyethersulfone/polyvinyl acetate blend membrane incorporated with TiO₂ nanoparticles for CO₂/CH₄ gas separation

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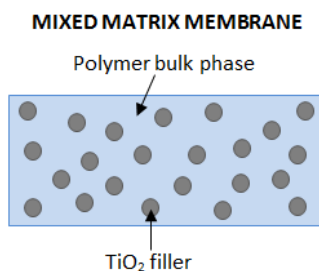
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Graphical abstract

MIXED MATRIX MEMBRANE

Abstract

Development of polymer blend membranes is gaining much attention especially for gas separation processes. This paper is primarily focused on synthesizing polymer blend membranes incorporated with titanium dioxide (TiO₂) nanoparticles as inorganic filler to enhance its performances. Polyethersulfone (PES) and polyvinyl acetate (PVAc) were blended at ratio of 90/10, together with 5 wt.% of TiO₂ in dimethylformamide (DMF). The morphological structure of the membrane was analysed via FESEM. It shows that a rigid/non-porous membrane with slight nanoparticles agglomeration was formed. As interpreted from TGA, incorporating TiO₂ nanoparticles into the polymer blend reduces the degradation temperature, increases wt.% of leftover residual thus proves an enhancement in thermal stability of the membrane. Moreover, the presence of TiO₂ nanoparticles in the developed membrane possesses some effect on the spectral analysis as observed via FTIR spectroscopy. The permeability of CO₂ gas is improved with addition of TiO₂ nanoparticles within the blend membrane and better selectivity of CO₂/CH₄ is observed.

Keywords: Polymer blend membrane, PES/PVAc, TiO₂ nanoparticles, inorganic filler, gas separation

INTRODUCTION

Membrane technology is widely being utilized in gas separation industries particularly for elimination of CO_2 from natural gas. This is due to the characteristics of the membrane itself which are light weight, environment friendly and compact size configuration which is suitable to be installed for offshore platform. In addition, it requires small capital and operating costs as well as low requirements of energy [1, 2]. Polymeric and inorganic membranes are the most commonly used membranes for such application. Polymeric membranes are made from either glassy or rubbery materials including polysulfone, polyethersulfone, polyvinyl acetate etc. Polymeric membranes possess the inability to withstand chemical degradation and thermal instability, thus limit their applications when face upon separation process involving hot reactive gases [3].

Therefore, combining two polymers of different types (glassy and rubbery) will produce new membrane material that can symbiotically merge the good traits of each polymer that are not attainable individually foremost in enhancing the gas permeability through the membrane [4]. By varying the composition of the blend, specific characteristics can be achieved for tailor-made applications [5]. Above all, membrane for gas separation is favourably to be dense in structure, where the solution-diffusion mechanism takes place. Polymers containing ether and carbonyl groups are attractive for carbon dioxide removal due to strong affinity between CO_2 and these groups [5, 6]. The binding modes exhibit in PES and PVAc monomer offers a prominence of the reliability for these two polymers to be a good material for CO_2 removal. The existence of carbonyl-oxygen and ester-oxygen in PVAc monomer offer three binding modes with CO_2 molecules, while ether-oxygen in PES monomer can accommodate one binding mode for CO_2 molecule [6]. Other than being advantageous at the molecular level, PVAc is a polymer of having medium glass transition temperature (T_g), easy film forming property, high solubility of CO_2 due to the polar acetate group exists in its structure, and commercially available in high commodity polymer [5, 7].

However, the limitation comes in term of fabrication. PVAc cannot be used individually for membrane fabrication due to its sticky nature when cast on glass plate [7]. Thus, it needs to be blend with glassy polymer that has high mechanical strength and can resist chemical instabilities [8]. PES is one of the most studied polymers as it offers good mechanical and resistivity towards harsh operating condition [9]. Combining glassy and rubbery polymers to develop polymer blend membrane was intended to improve its performance by drawing the advantages from the parent polymer specifically the individual gas separation features, together with the molecular aspect which is to provide more binding mode with carbon dioxide. Besides, generally, unmodified polymeric membranes are suffering from limitation to cross the Robeson's upper boundary due to the trade-off in between selectivity and permeability [9].

Polymer blend is an attractive alternative in the synthesis of membrane for gas separation, but the key challenge of this method is to achieve compatibility between the polymers pair used, as well as retaining the desired mechanical properties [9]. Previous blend studies reported the immiscibility in the blend, which at the molecular stage affected the physical and chemical properties of the membrane though

still there is commercialized immiscible blend, but they often exhibit unstable phase morphology during melt processing resulting in poor mechanical performance [10, 11].

A study on blending PES and PVAc has been conducted recently and it turns out that the structural properties as well as the performance the developed membrane needed to be optimized further [12]. Hence, this project is carried out to synthesis PES/PVAc blend membrane incorporated with TiO_2 as inorganic filler. The effect of TiO_2 nanoparticles on physico-chemical properties and gas separation performance of the blend membrane is also to be investigated. TiO_2 is selected to act as filler to the polymer blend as well as a key parameter to improve the co-continuous morphology of the blend. The nanoparticles have better hydrophilicity, high stability, less expensive, non-toxic, and can easily be dispersed [13-15]. TiO_2 nanoparticles are agents which could speed up the rate of growth on the membrane formation mechanism [14]. Higher energy will be needed to disintegrate the bonding between polymers and TiO_2 when the nanoparticles act as a crosslinking point to connect the polymer chain and increase its rigidity. The resultant membrane is to be analysed for the morphological structure, thermal stability, infrared spectroscopy, along with CO_2/CH_4 gas permeation studies. In this study, three different membranes were presented for comparison with each other; pure PES, PES/PVAc blend, and PES/PVAc blend incorporated with 5 wt.% TiO_2 nanoparticles.

EXPERIMENTAL

Materials

PES flakes (ULTRASON® E-6060 P with Mw=50000g/mol) were first desiccated in oven at 100°C for 12 hours before using to remove moisture. PVAc beads (Mw=100,000g/mol) were used in raw form (no prior drying to be done). The N,N-Dimethylformamide (DMF) EMPLURA® as the inorganic solvent was purchased from Merck Germany. The Titanium (IV) dioxide (TiO_2) nanoparticles with 21nm primary particle size were purchased from Sigma Aldrich.

Membrane synthesization

In this study, three different membranes were fabricated for comparison; pure PES, PES/PVAc blend, and PES/PVAc blend incorporated with TiO_2 nanoparticles. The ratio of PES/PVAc polymer blend was standardized at 90/10 as per accordance to the optimized polymeric membrane ratio [16]. The optimum polymer concentration was determined to be 20 wt.% of the solvent, whereas the nanoparticle concentration is 5 wt.% of the total polymers. The nanoparticles were initially dissolved in DMF and the solution was stirred for 1/2 hour for homogenization. The TiO_2-DMF solution was ultrasonicated for another 1/2 hour to effectively disperse the TiO_2 particles within the solvent. 10% of the polymers were added subsequently into the solution and then stirred for 1 hour at 40°C. The remaining polymers were later added and the stirring process continued overnight. The membrane solution was poured on a half A4-sized glass plate and cast using casting knife with thickness of 100μm. The membrane film was left in an aluminium foil covered tray for 4 hours. The drying process of the cast membrane was done in an oven at 90°C for 24 hours.

Characterization of membranes

Variable Pressure Field Emission Scanning Electron Microscope (VPFESEM, Zeiss Supra55 VP) was applied to analyze the structural morphologies of the cross-sectionals and surfaces of the membranes. For the cross section images, the membrane samples were soaked in liquid nitrogen for 5 minutes before they were cracked afterward. Thermogravimetric analysis was done to study the thermal stability of the developed membranes by using Perkin Elmer TGA (Pyris 1) system under 20 ml/min of N_2 flow, from 30 – 800°C at ramp rate of 20°C/min. Fourier transform infrared spectrometer (Perkin-Elmer® Spectrum one FT-IR Spectrometer) had been utilized to explore the interaction between polymers and the nanoparticles and to analyse the functional groups present. The wavelength used is in range of 4000 to 500 cm^{-1}.

Gas permeation test

The synthesized membranes were tested for permeability of pure (99.99%) carbon dioxide (CO_2) and methane (CH_4) using the pre-installed gas permeation unit. The pressure and temperature of the setup were set at 10 bar and 25°C respectively. Prior testing, any residual gases within the unit were evacuated by using a vacuum pump. The pressure at the permeate side was set to be constant at atmospheric pressure. A bubble flow meter which can detect flow rates as low as 100 ml/min was used to measure the permeation rate of gas streams. The equation to calculate permeation of gas is as follow:

$$P_i/L = J_i/\Delta p_i \qquad (1)$$

Where L is the membrane thickness, J_i represents the gas flux, whereas Δp_i is the transmembrane pressure drop. On the other hand, selectivity of the membrane will be calculated by following equation:

$$\alpha_{CO2/CH4} = P_{CO2}/P_{CH4} \qquad (2)$$

RESULTS AND DISCUSSION

FESEM analysis

In this study, the flat sheet membrane of PES/PVAc blend incorporated with TiO_2 was synthesized by dry phase inversion method. The thickness of pure PES membrane is 25 μm whereas PES/PVAc blend and PES/PVAc-TiO_2 have membrane thicknesses of 93.4 μm and 71.5 μm respectively.

Fig. 1 and Fig. 2 show the FESEM images indicating the morphologies of top layer and cross-section (1000x magnification) of the developed mixed matrix membranes together with PES and PES/PVAc blend membranes. The surface of pure PES and PES/PVAc blend membranes are shown in Fig. 1a and Fig. 1b respectively. It is confirmed that both membranes are smooth and homogenous as there is neither defect nor pore formed on both surfaces. Fig. 1c displays the morphology of the PES/PVAc-TiO_2 membrane. It can be seen that the surface is also smooth and no pores detected. Nevertheless, weak aggregation of TiO_2 nanoparticles can be spotted within the membrane (marked with blue circles). Previous studies also reported the same situation where severe aggregation were visible after increasing nanoparticles concentration [17, 18].

In Fig. 2a, the pure PES membrane seems to have a rigid structure and no pore is observed while Fig. 2b of PES/PVAc blend expresses otherwise. A nodular structure of two-phase morphology is visible. Particles of minor phase (PVAc) as depicted in red circles are dispersed in the major one (PES matrix) which might be due to the incompatibility between the polymer pair. Similar observation was also reported by other researchers [19]. Fig. 2c somehow shows a rigid and dense structure of the mixed matrix membrane. The presence of TiO_2 diminishes the size of dispersed particles. This phenomenon occurs due to good adhesion between PVAc with inorganic fillers specifically TiO_2 nanoparticles [7]. The morphology and rigidity of the mixed matrix membrane differs from other membranes due to the dispersion of TiO_2 nanoparticles within its structure [20].

Thermal analysis

TGA was applied to analyse the thermal stability of the membranes. The TGA graph for PES, PES/PVAc and PES/PVAc-TiO_2 is shown in Fig. 3. Initial weight loss observed at 200°C is associated to the release of leftover solvent. Neat PES membrane begins to decompose rapidly at 493°C and it continues until 592°C. The rapid decomposition temperature of PES/PVAc blend membrane starts at temperature of 507°C until it reaches 598°C. Concurrently, the mixed matrix membrane (PES/PVAc-TiO_2) starts to decompose at 525°C and the temperature of final decomposition is recorded at 594°C.
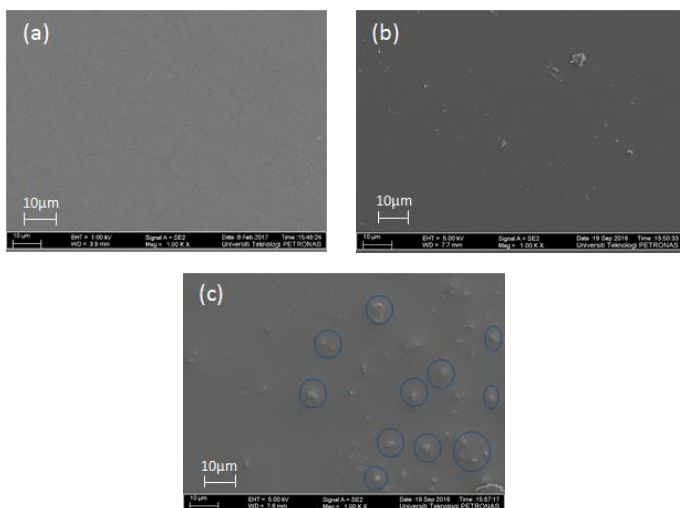
Fig. 1 Surface images of a) pure PES, b) PES/PVAc blend, and c) PES/PVAc-TiO$_2$ membranes
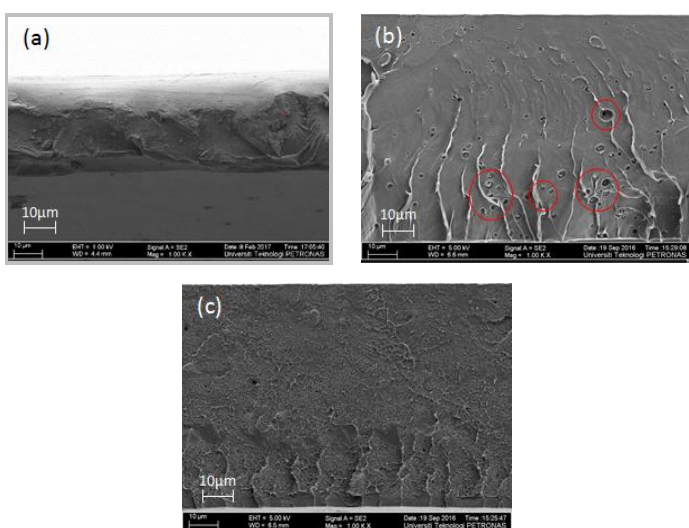
Fig. 2 Cross-sectional images of a) pure PES, b) PES/PVAc blend, and c) PES/PVAc-TiO$_2$ membranes

After being decomposed until 800°C, the residue left in the mixed matrix membrane is the highest which is 43% compared to neat PES (28%) and PES/PVAc polymer blend (35%). Adding TiO$_2$ nanoparticles into the polymer blend reduces the degradation temperature, increases wt% of residue left thus proves an enhancement in thermal stability of the membrane. These findings are in good agreement as per reported in other studies [7, 14, 17].
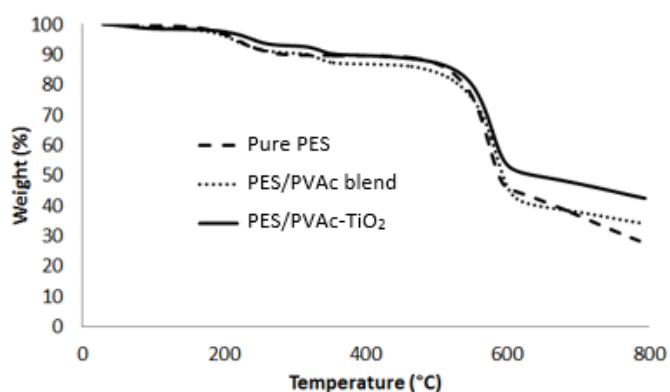
Fig. 3 TGA curve of pure PES, PES/PVAc blend, and PES/PVAc-TiO$_2$ membranes

FTIR analysis

The FTIR spectra of the pure PES, PES/PVAc blend, and PES/PVAc-TiO$_2$ membranes are described in Fig. 4. All three membranes show somewhat similar spectral trend from 1700 cm^{-1} to 600 cm^{-1}. The characteristic peaks for the all three membranes are not much difference to the ones justified in previous study [8]. No significant movement in the line spectrum of the mixed matrix membrane throughout the wavenumber regions even with the presence of TiO$_2$ nanoparticles in the membrane surface. However higher peaks can be seen from the spectra of mixed matrix membrane at band range of 1107 cm^{-1} to 1305 cm^{-1} and 1480 cm^{-1} to 1675 cm^{-1} compared to the other membranes. This might be due to interactions of TiO$_2$ nanoparticles with the sulfone groups (O=S=O), benzene groups and ether oxygen in the polymer structure. It is observed that the peaks at 1800 cm^{-1} to 2230 cm^{-1} disappear for the PES/PVAc-TiO$_2$ membrane. The reason is that incorporation of TiO$_2$ nanoparticles into the blend membrane changes the colour of the membrane and turns it into opaque (both pure PES and PES/PVAc blend membranes are transparent), thus affecting the spectral transmittance of light through the membrane samples.
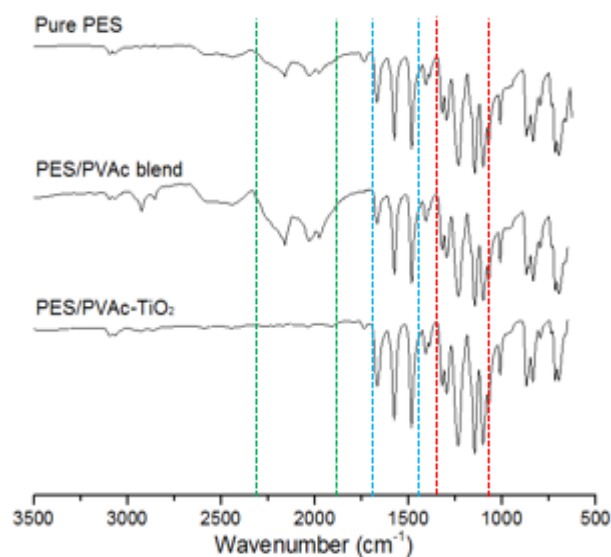
Fig. 4 FTIR spectra of pure PES, PES/PVAc blend, and PES/PVAc-TiO$_2$ membranes

Gas permeation test

Fig. 5 and Fig. 6 display the results of permeabilities and selectivities for pure PES, PES/PVAc blend, and PES/PVAc-TiO$_2$ membranes. As seen from the figures, the mixed matrix membrane has superior performance compared to the other membranes. The permeance of CO$_2$ and CH$_4$ recorded for the neat PES membrane is 15.35 GPU and 10.45 GPU respectively. The permeance of CO$_2$ gas increases for the PES/PVAc blend membrane as it recorded a value of 15.78 GPU while permeance of CH$_4$ decreases (8.12 GPU). Significant increment of CO$_2$ and CH$_4$ permeability can be seen when the polymer blend membrane incorporated with TiO$_2$ nanoparticles has recorded permeance of 20.32 GPU and 8.33 GPU respectively. The CO$_2$/CH$_4$ selectivity for the mixed matrix membrane is the highest (2.44) as compared to the pure PES (1.47) and PES/PVAc blend (1.94) membranes. Nonetheless, it still unable to surpass the designated Robeson's upper boundary and still beneath the performance of currently commercialized membranes. The addition of TiO$_2$ into the PES/PVAc polymer blend has caused nanoparticles aggregation and increased the formation of free volume void in between TiO$_2$-polymers interface, thus allow better diffusivity of gases through the membrane [20].
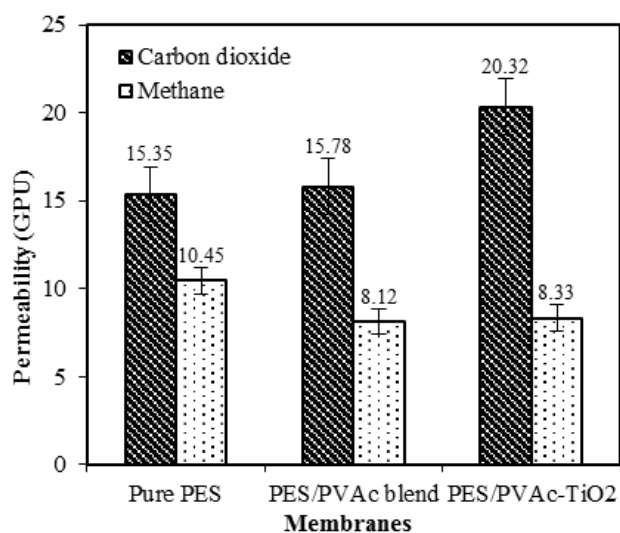
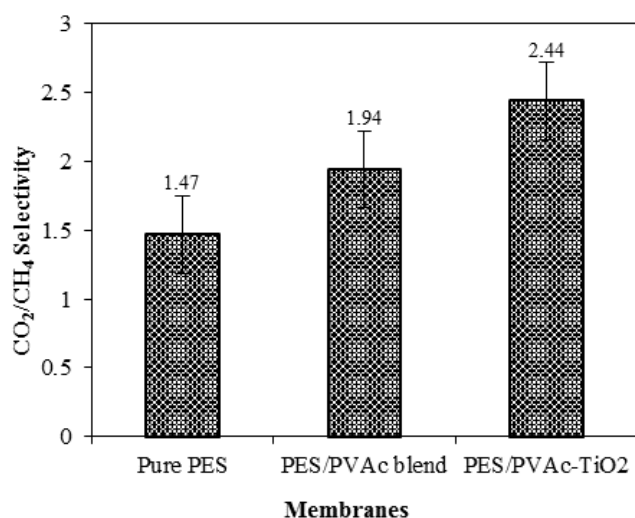**Fig. 5** CO_2 and CH_4 gas permeabilities.

Fig. 6 Ideal gas selectivity.

CONCLUSION

PES/PVAc blend membrane incorporated with 5 wt.% of TiO_2 nanoparticles is synthesized in this project work. The role of TiO_2 nanoparticles is to act as inorganic filler and enhance the properties of the mixed matrix membrane. The smooth and rigid morphological structure of the mixed matrix membrane shown by FESEM indicates a homogenous interaction between the polymers and TiO_2 nanoparticles. However, the aggregation of TiO_2 nanoparticles seemed to be visible. The thermal stability of the mixed matrix membrane is better as the wt.% of leftover residue is the highest as compared to the neat PES and PES/PVAc blend membrane. From the FTIR spectroscopy results, the presence of TiO_2 had caused increase of peaks for certain functional groups which demonstrate the good interaction between the polymers and TiO_2 nanoparticles. The results of CO_2 permeability and CO_2/CH_4 selectivity recorded by the mixed matrix membrane are better than the pure PES and PES/PVAc blend membranes.

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