AN INVESTIGATION ON POLYMERIC BLEND MIXED MATRIX MEMBRANES OF POLYETHERSULFONE/POLYVINYL ACETATE/CARBON MOLECULAR SIEVE FOR CO2/CH4 SEPARATION

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ABSTRACT

Polymeric membranes have been vastly used for gas separation purposes however they have an upper-bound trade off problem which is the reason why this research work is focusing on inorganic filler added to polymer blend membranes to enhance the selectivity and permeability of the resulted membranes. Different percentages (5, 10 and 15 wt.%) of carbon molecular sieve (CMS) were added to a blend of polyethersulfone/polyvinyl acetate (PES/PVAc) (90/10) to produce polymeric blend mixed matrix membranes (PB3M) by solvent evaporation method. These membranes were characterized by field emission scanning electron microscopy (FESEM) to find out the membrane morphology and then their gas separation performance was assessed using high purity CO_2 and CH_4 gases. Addition of CMS to the blend of this glassy and rubbery polymer, increased the CO_2/CH_4 selectivity and CO_2 permeability of the resulted PB3Ms. The highest selectivity which was 43.26 was achieved at 10 bar and at room temperature by adding 15% CMS to the polymer blend membrane.

Keywords: Mixed Matrix membrane; polyvinyl acetate; polyethersulfone; carbon molecular sieve

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1. INTRODUCTION

Membrane is a thin layer which separates two phases and limits transport of different materials in a selective manner. Membrane technology is a developing field as membrane separation process possesses more advantages over other separation technologies e.g., easy operation, low cost, low energy consumption, low maintenance, low labor intensity, environmentally friendly and also without any corrosion [1]. For gas separation purposes, membranes own the highest ability. The best performance of a membrane is when both gas permeability and selectivity are high without having any upper-bound trade off which happens in polymeric membranes. Membrane separation approach has a lot of advantages; one of which is its cost-effectiveness that plays a very crucial role in industry. There are other merits to membrane technique such as low capital investment, low weight, low space requirement and high process flexibility. Membrane gas separation method has been widely used recently and can be considered as a competitive industrial gas separation technology [1-4].

Polymeric membranes have been produced for a wide range of industrial applications including gas separation. However, the performance of polymeric membranes in Carbon dioxide removal of Methane is not very good as it shows an inverse relationship between permeability and selectivity. One of the techniques to enhance the properties of a polymer is by blending it with another polymer that possesses some desired physical and chemical properties. In comparison to other enhancement techniques or even with the synthesis of completely novel materials from the start, polymer blending is preferred owing to its simplicity, reproducibility and commercial character [5-9]. A blend can show new properties not found for single polymers. This also holds for membrane preparation to tailor a specific separation performance. Furthermore, blending is an option for reducing the price of the membranes [4]. On the other hand, another method to improve the properties of polymeric membranes is to add an inorganic filler to it which is called mixed matrix membranes (MMMs) that are aimed to improve the polymeric membrane separation performance. These membranes are usually developed by incorporation of high separation performance inorganic molecular sieves in polymer matrices. The merits of polymeric membranes and the superior separation performances of molecular sieves are mixed in MMMs [10, 11].

Polyethersulfone was used as the polymeric base for membranes because of its good heat

resistance, good creep resistance and also shows satisfactory performance at high temperatures [12]. In a study by Li et al. [13], the polyethersulfone (PES)-zeolite 3A, 4A and 5A mixed matrix membranes (MMMs) were fabricated with a modified solution-casting procedure at high temperatures close to the glass transition temperatures (Tg) of polymer materials. The experimental results indicated that a higher zeolite loading resulted in an increase in gas permeability and gas pair selectivity. In another effort, Ismail et al. [14] investigated the gas separation performance of mixed matrix membranes flat sheet based on Polyethersulfone/Polyimide (PES/PI) miscible blend incorporated with Zeolite particles. They concluded that addition of Zeolite particles into the matrix of PES/PI polymer blend has significant effect on the membrane structure and properties. In a study by Vu et al. [15], Carbon molecular sieves (CMS) were incorporated into

two different polymer matrices to develop mixed matrix membrane films for gas separation purposes; Polyimide (Matrimid) and polyetherimide (Ultem) mixed matrix membranes synthesized in that study, displayed significant enhancements in both CO_2/CH_4 and O_2/N_2 selectivities and also permeabilities of the fast-gas penetrants (O_2 and CO_2) through the mixed matrix membranes were significantly enhanced in comparison with the intrinsic permeabilities of polyimide and polyetherimide matrices.

In this research study, two aforementioned methods of improving polymeric membranes were combined and a new type of membrane which is called polymeric blend mixed matrix membrane (PB3M) was synthesized and then characterized by FESEM and its performance for CO_2/CH_4 separation was evaluated.

2. RESULTS AND DISCUSSION

2.1. Field Emission Scanning Electron Microscope (FESEM)

FESEM images are shown in Figure 1. In order to obtain the cross-sectional membrane structure, all the samples were prepared by breaking them in liquid Nitrogen. In Figure 1, the morphology of cross-sectional images of the resulted membranes revealed the dense and smooth structure of them. The thickness of the developed membranes was 47.46μm for pure PES, 53.61μm for polymer blend of PES/PVAc, 52.38μm for PB3M_5, 47.91μm for PB3M_10 and 74.94μm for PB3M_15. As can be seen from Figure 1, in PB3Ms, CMS was

dispersed homogenously all over the blend membrane with no major agglomerations which is due to the good membrane preparation techniques and acceptable interactions between these three materials.

(a)

(b)

(c)

(d)

(e)
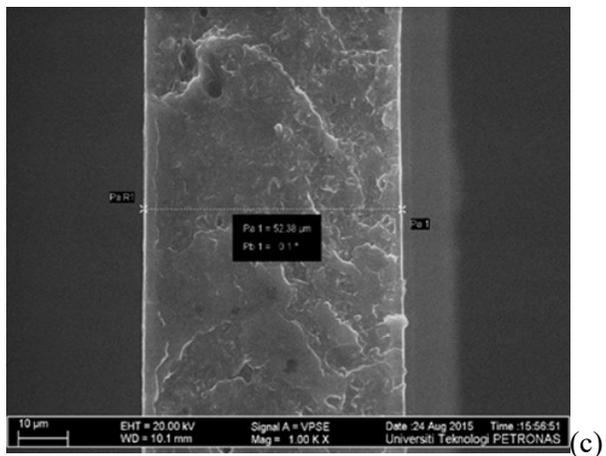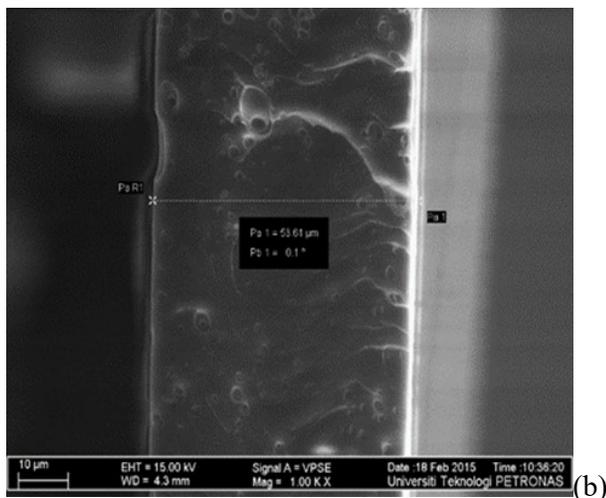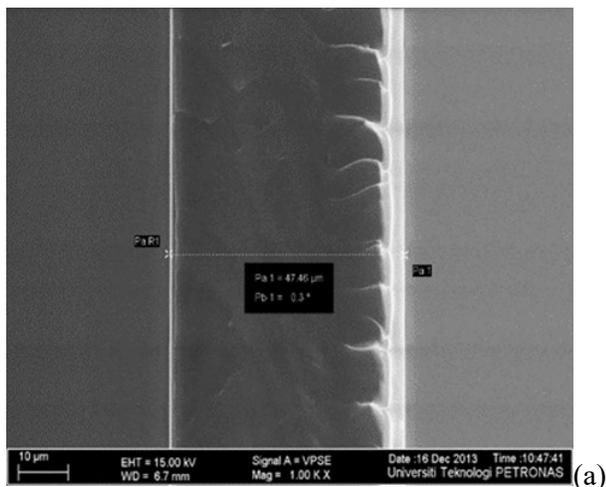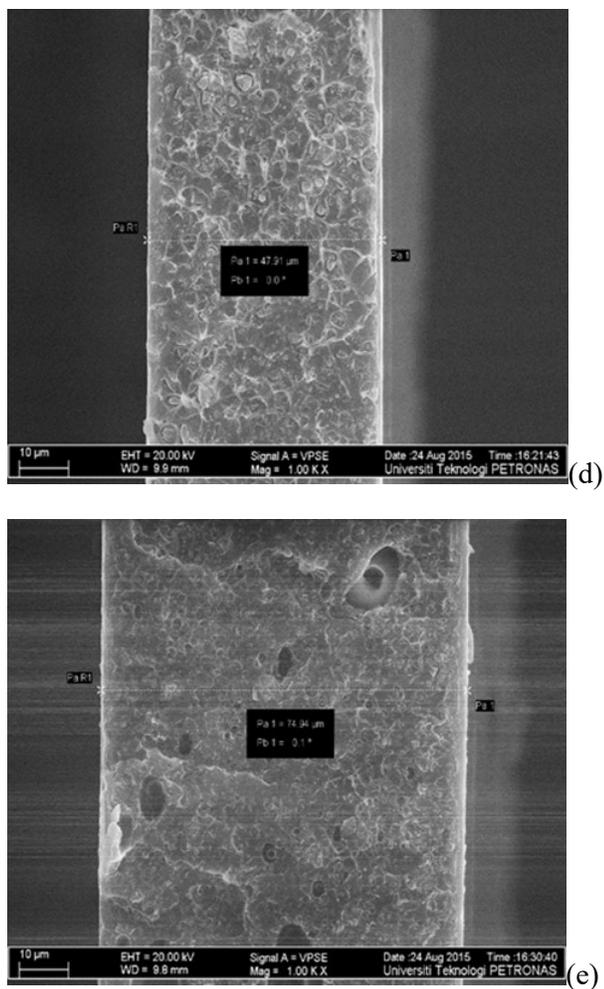
Fig.1. FESEM cross-sectional images of a) pure PES membrane, b) polymer blend, c) PB3M_5, d) PB3M_10, and e) PB3M_15

There were some small voids in blend polymeric mixed matrix membranes which could be attributed to the interfacial regions appeared around CMS particles which formed a loose structure resulting in a small void.
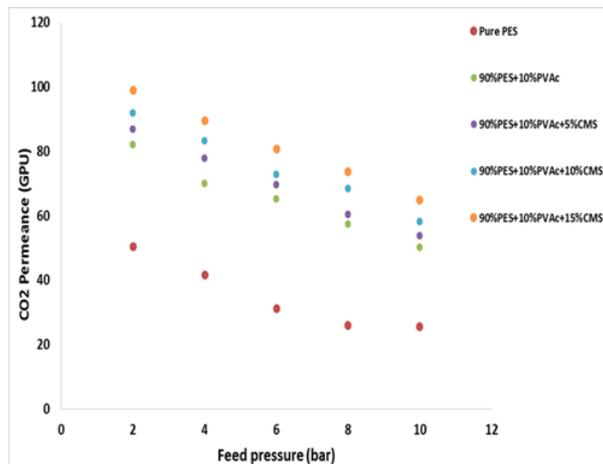
Fig.2. Permeance of single CO2 gas in developed membranes as a function of pressure
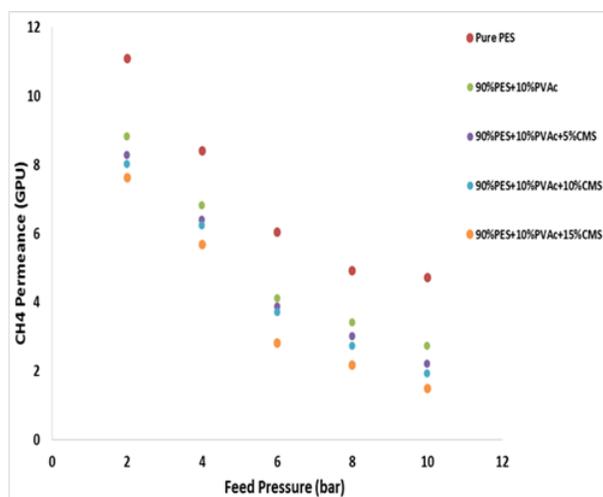

Fig.3. Permeance of single CH4 gas in developed membranes as a function of pressure
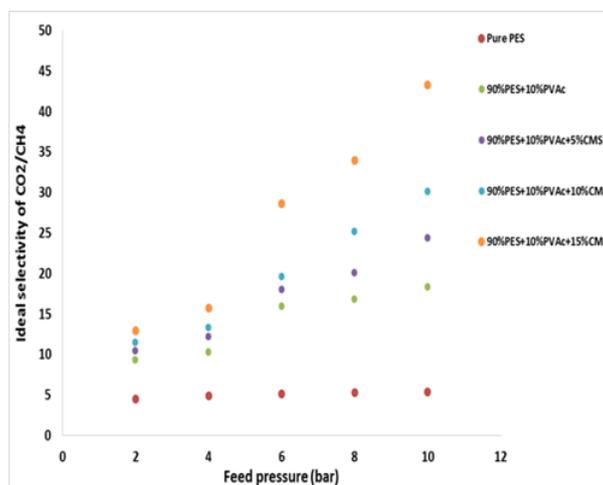

Fig.4. CO2/CH4 ideal selectivity in developed membranes as a function of pressure

2.2. Gas Permeability Study

The gas permeance and selectivity studies of CO_2 and CH_4 gases for pure PES membrane as well as the blended sample and PB3Ms are shown in Figure 2, 3 and 4. It is observed in Figure 2 that the CO_2 permeance of pure PES membrane increased by adding PVAc to it and then when CMS was added to the blend of PES/PVAc, still the CO_2 permeance kept going high until for PB3M_15, it reached

its highest amount which was 64.89 GPU that is 154% greater than that of pure PES.

As it is indicated by Figure 3, CH_4 permeance of PB3M membranes is decreasing by increasing the CMS loading because CMS kinetic diameter (3.8oA) is near the CH_4 (3.8oA) kinetic diameter but higher than that of CO_2 (3.3 Å) so CO_2 molecules can pass through it much easier than CH_4 [17].

Therefore, ideal selectivity of CO_2/CH_4 for these membranes that is portrayed in Figure 4, rose by increasing the CMS amount. The highest selectivity was gained for PB3M_15 at 10 bar which was 43.26. It was seen that there was an increase of CO_2 permeance and ideal selectivity when adding CMS particles to the polymer blend. As expected, the addition of CMS particles increased the CO_2 permeance and CO_2/CH_4 selectivity and diminished CH_4 permeance.

By increasing the feed pressure, the permeance decreased for all the membranes and selectivity increased as the main phase is PES which is a glassy polymer and in glassy polymers, by increasing the feed pressure, gas permeance goes down while selectivity rises [18, 19].

3. EXPERIMENTAL

A. Materials

Polyethersulfone (PES) (ULTRASON E 6020P) was purchased from BASF Germany having a molecular weight of 50,000 g/mol. PES was the main polymer for the fabrication of PB3Ms. Polyvinyl acetate (PVA_c) beads (Mw=100,000g/mol), supplied by Sigma Aldrich were used as received. Dimethylformamide (DMF) was purchased from Merck Germany and used as the solvent for preparation of membrane solutions. The inorganic filler, CMS was purchased from Japan Enviro Chemical.

B. METHODOLOGY

Firstly, pure Polyethersulfone (PES) membrane casting solution was prepared using dope solution method in a way that PES flakes were added to the solvent (DMF) slowly and was stirred with a magnetic stirrer for 24 hours to gain a homogenous solution; after that they were ultrasonicated for 30 mins; then all the membranes were cast using membrane casting machine. Membrane dope solution was poured on the glass plate that had been located under the casting knife. Right after that, membrane was dried in the oven for 2 hours at 100°C. For the blend sample, membrane casting solutions were produced by first blending the weighed PVA_c and DMF. PVA_c and DMF mixture was stirred slowly until a clear solution was achieved. Then, weighed PES was slowly added to the solution and the mixing was continued for the whole night to make sure a homogenous mixture was obtained. For polymeric blend mixed matrix membranes` production, the same procedure was followed with the difference that first CMS was added to the solvent and stirred for 24 hours and the rest of methodology was just followed like preparation of blend membranes.

Table 1. demonstrates the dope solution compositions for all produced membranes.

Membrane	Glassy Polymer (PES) (wt%)	Rubbery Polymer (PVA_c) (wt%)	Carbon Molecular Sieves (CMS) (wt%)
Pure PES	100	0	0
Polymer Blend	90	10	0
PB3M_5	90	10	5
PB3M_10	90	10	10
PB3M_15	90	10	15

C. Characterization of Membranes

FESEM test (Zeiss SUPRA™55VP) was carried out for all the resulted membranes.

Cross-sectional FESEM images were employed to evaluate the existence of any fracture or void in membranes.

D. Gas Permeability Study

The permeability experiment was conducted using a gas permeation unit at feed permeate pressures from 2 to 10 bar and room temperature. The permeance of the test gases which were pure CO_2 and CH_4 was calculated using the following equation:

$$P_i/l = J_i/\Delta P_i \tag{1}$$

where P_i is the permeance of the gas, J is the flux of the gas, l represented membrane thickness and Δp is the pressure difference.

The ideal selectivity of the membrane is achieved by the below equation:

$$\alpha_{CO2/CH4} = P_{CO2}/P_{CH4} \tag{2}$$

4. CONCLUSION

Pure PES membrane, one blended membrane containing a rubbery and a glassy polymer (PES/PVA$_c$) and PES/PVA$_c$/CMS polymeric blend mixed matrix membranes were prepared in this study. Their FESEM results showed a dense non-porous structure for all the membranes and also CMS demonstrated no agglomeration in the blend polymeric mixed matrix membranes. By adding more CMS, CO_2 permeance and CO_2/CH_4 selectivity increased to 64.89 GPU and 43.26 GPU from 25.54 GPU and 5.41 GPU for pure PES at 10 bar feed pressure respectively however CH_4 permeance diminished to 1.5 GPU from 4.72 GPU for pure PES at 10 bar feed pressure.

5. ACKNOWLEDGEMENTS

6. REFERENCES

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