Studies on gas separation behaviour of polymer blending PI/PES hybrid mixed membrane: Effect of polymer concentration and zeolite loading

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Abstract - *This study is performed primarily to investigate the effect of polymer concentration of polyimide/polyethersulfone (PI/PES) blending on the gas separation performance of hybrid mixed matrix membrane. In this study, PI/ (PES)–zeolite 4A mixed matrix membranes were casted using dry/wet phase inversion technique. The efefct of PI/PES concentrations and zeolite loading on the dope solution were investigated for gas separation performance. The results from the Field Emission Scanning Electron Microscopy (FESEM) analysis confirmed that polymer concentration and zeolite loading was affected the morphology of membrane and gas separation performance. 'Sieve-in-a-cage' morphology observed the poor adhesion between polymer and zeolite at higher zeolite loading. The gas separation performance of the mixed matrix membranes were relatively higher compared to that of the neat polymeric membrane.*

Keywords — *mixed matrix membrane, polymer blending, zeolite membrane gas separation*

I. INTRODUCTION

The gas separation process by polymer membranes for natural gas processing, landfill gas recovery, air separation and hydrogen recovery have received much attention during the past several decades. The important factors affected application of membrane in gas separation such as feed composition, membrane materials, membrane configuration, plant capacity and operating costs. Currently, many researchers have focused studies on mixed matrix membrane to enhance gas separation performance. Hybrid membranes or mixed matrix membrane concept combines the advantages of high separation capabilities of the molecular sieves and the desirable mechanical properties and economical processing capabilities of polymers. Many studies have reported that the separation performance of mixed matrix membrane could be improved by integrating porous or nonporous inorganic filler such as zeolite, silica, carbon molecular sieve and activated carbon (Süer et al., 1994, Duval et al., 1994; Vankelecom et al., 1996 Zimmerman et al., 1997, Ismail et al 2008 and Kusworo et al 2008). Although the interphases on zeolite (inorganic composites) occupies an extremely small volume fraction (i.e., less than 10 %), it appears to have a significant effect on the separation performance of mixed matrix membranes (Süer et al., 1994). The origins of the imperfect interphases are complicated. Poor compatibility between molecular sieve and polymer matrix where by the tendency to develop voids between polymer and zeolite phases are very high, uneven shrinkages and stresses of these two components during the membrane formation may be some of the possible causes. Süer et al. (1994) also stated in their previous

studies that, polymer chain rigidification and partial pore blockage of zeolites have been hypothesized and partially confirmed to form the lower gas permeation data of mixed matrix membranes. Nevertheless, previous studies (Duval et al., 1994 and Ismail et al., 2008) have identified difficulties in obtaining good polymer–sieve contact with rigid, glassy polymers, such as polyimides. Such glassy polymer mixed matrix membranes often demonstrated poor polymer–sieve adhesion, resulting in macroscopic voids and no selectivity enhancement. Thus, appropriate selection of the sieve and the percent of loading is an important consideration to match the fast-gas permeability (Mahajan and Koros, 2000). Kusworo et al. (2008) concluded that the major problem of mixed matrix membranes using glassy polymers is adhesion between the polymer phase and the external surface of the particle. It seems that the weak polymer-filler interaction makes the filler tend to form voids in the interface between the polymer and filler. Hence, the resultant membranes generally have deteriorated selectivity. Moreover, it is important to overcome these challenges that prevents successful introduction of inorganic molecular sieve materials into an organic polymer matrix. Sieve-in a-cage is one of example problem on the fabrication of mixed matrix membrane, where a void exists at the polymer-sieve interface in the morphology of mixed matrix membrane. As the void size increases, the permeability increases while the selectivity near one. Therefore, in this paper discussed an alternative preparation of mixed matrix membrane using polyimide and polyethersulfone blends for CO_2/CH_4 separation with different loading of zeolite 4A as inorganic filler. The effects of preparation conditions such as temperature processes, polymer concentration and zeolite loading on the dope solution were also investigated.

II. EXPERIMENTAL

2.1 Material selection

Polyimide (Matrimide 5218) resin was supplied by Alfa Aesar Johnson Mattew Mexico and polyethersulfone by Solvay Advanced Material (USA). The polymers were dried in a vacuum oven at 120 oC overnight before dope preparation; N-methyl-pyrrolidinone (NMP) from Merck was used as the solvent due to its low toxicity. The inorganic filler molecular sieve involved was zeolite 4A from Aldrich and the particle size was 1 μm. In order to remove the adsorbed water vapour or other organic vapors, all zeolite particles were dehydrated at 300 oC for 3 hours before use.

2.2. Fabrication of asymmetric polyethersulfone-carbon nanotubes mixed matrix membrane

Ahead of preparing the dope solution, all the equipments needed were dried in the oven to remove water moisture. In this study, the polymer solution was consisted of 15-30wt % polymer (blend PI/PES, 20/80), and 75 % NMP + 10-50wt % zeolite loading in total solid.

Mixed matrix dopes are prepared as two parts: a sieve suspension and a polymer solution which are then mixed together. The sieve suspension is typically of low viscosity, whereas the polymer solution is concentrated and highly viscous. This is necessary to produce casting dope in approximately 15 %-25 % total solids. The homogeneous polyimide and polyethersulfone were prepared according to the following procedure; the inorganic molecular sieve particles were dispersed into the solvent and stirred for 24 hours than followed by the addition of a desired amount of polyimide. The solution was agitated with a stirrer at least 24 hours to ensure complete dissolution of the polymer. Next, a desired amount of polyethersulfone was added to this homogenous solution. This solution was further agitated by stirring at high speed for at least 2 days to form homogenous solution and at 60 oC.

2.3. Post-treatment procedure

The membrane sheets were coated with highly permeable elastomeric silicone polymer (Sylgard 184 Dow Corning). The membrane coating was done after the uncoated membranes were tested. The intention of coating is to fill any surface pinholes or defects on membrane surface. Membranes were submerged in the 3% w/w solution of silicone in n-hexane for 24 hours and subsequently placed in oven for 3 days at 120 oC to allow curing before permeation testing.

2.4. Module fabrication and gas permeation experiment

The permeation test involved the use of gas permeation cell in which the membrane was placed on a sintered metal plate and pressurized at the feed side. Gas permeation rates were measured by a constant pressure system using a soap bubble flow meter. Figure 1 illustrates the gas permeation cell set up. The cross-membrane pressure difference was maintained 10 bar.
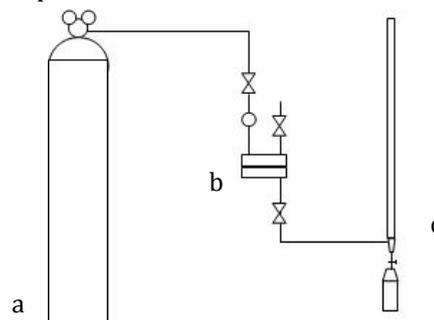
Figure 1: Gas permeation test cell; (a) gas silinder, (b) membrane cell, (c) buble soap

The permeability can be calculated using the following equation 1:

$$(P) = \frac{Q_i l}{(\Delta p)(A)} \qquad (1)$$

where Qi is the volumetric flow rate of gas "i" at standard temperature and pressure, Δp is the transmembrane pressure difference, l is the membrane thickness and A is the effective membrane area. Permeability is expressed in barrers (1010 cm3 (STP) cm/cm2 s cm Hg). The ideal separation factor can be calculated using the following equation 2:

$$\alpha_{i/j} = \frac{(P)_i}{(P)_j} \qquad (2)$$

III. RESULTS AND DISCUSSION

3.1. Effect of polymer concentration on the morphology and gas separation performance of mixed matrix membranes

The permeabilities for pure gases CO2, and CH4 and the calculated ideal separation factor for CO2/CH4 gas pairs for different polymer concentrations of PI/PES - zeolite mixed matrix membranes are tabulated in Table 1. The dense layer of PI/PES blend matrix, highly selective zeolite sieve and non-selective gaps or voids between the matrix and sieve particles are the three main pathways of gas transport through the mixed matrix membrane. The permeability and selectivity values for 15 wt% polymer concentration for all gases were very low. These might be an indication of the Knudsen diffusion behaviour resulted in the membrane due to the presence of severe voids between zeolite particles and agglomeration as shown in Figure 2-3. Generally, Knudsen-diffusion controls the permeation of gas through porous membrane and the selectivity for binary gas in Knudsen-diffusion is given by equation 3.

$$\alpha_o = \left[\frac{M_A}{M_B}\right]^{1/2} \qquad (3)$$

where MA and MB are the molecular weights of component A and B, respectively. Equation 3 indicated that Knudsen-diffusion does not offer attractive separation factors, especially for gases of comparable molecular weight. The previous study of Vu et al. (2003) suggested that sedimentation of molecular sieve particles usually was caused by low viscosity of mixed matrix slurries. As supported by the FESEM in Figure 2-3, the gas transport could occur through the submicron gaps between the polymer matrix wall and the zeolite particles. As the gas transport through those unselective voids, it had been assumed to be the Knudsen diffusion behaviour, the permeability of CO2 became larger and exceeded the degree of increment of CH4 permeability due to gas flowing through the zeolite particles. Therefore, the selectivity of the resulted membrane was lower than that of the neat polymer. When the polymer concentration was above 25 wt%, the selectivity values were above the selectivity values of PI/PES neat membrane.

Table 1: Effect of polymer concentration on gas separation performance of 20/80 PI/PES- 25 wt% zeolite 4A mixed matrix membrane

Polymer concentration	Permeability (Barrer *)		Selectivity CO₂/CH₄
	CO₂	CH₄	
15 wt%	23.45 ± 0.35	6.78 ± 0.03	3,45
25 wt%	5.02 ± 0.23	0.11 ± 0.05	46.05
30 wt%	4.74 ± 0.01	0.11 ± 0.03	43.65
neat	6.54 ± 0.15	0.19 ± 0.01	33.59

* Barrer = 1 x 10^{-10} cm³ (STP) cm/cm² s cmHg
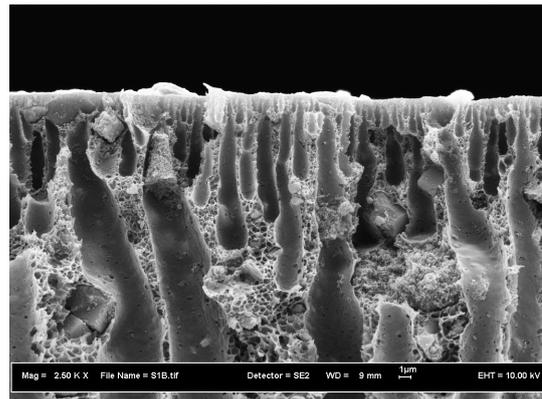
Figure 2: Cross-section images of PI/PES-zeolites 4A mixed matrix membranes with 15 wt% polymer
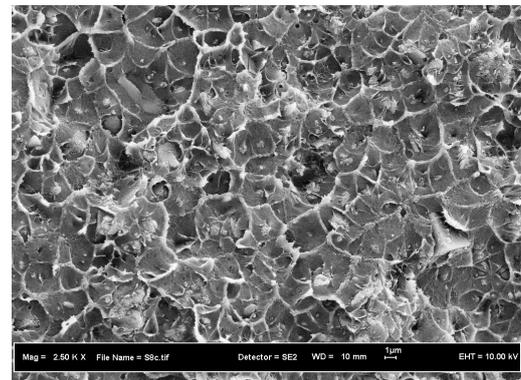
Figure 3: Surface images of PI/PES-zeolites 4A mixed matrix membranes with 15 wt% polymer

3.2. Effect of zeolite loading on the gas separation performance of mixed matrix membranes

The effects of zeolite loading on the morphology and performance of mixed matrix membrane are presented in Figures 4-6 and Table 2, respectively. From the Table 2, it can be observed that the permeabilities of CO2, and CH4, decreased up to a loading of 25 wt % of zeolite 4A. Above these loadings, a recovery in permeabilities started to occur. However, only moderate decrease in of CO2/CH4 selectivity was observed. The increase in permeability and the slight decrease in selectivity indicate that the PI/PES-zeolite mixed matrix membranes can be potentially used as a material membrane for commercial gas separation application.

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Table 2: Effect of zeolite 4A loading on the gas separation performance of 25wt % PI/PES (20/80) mixed matrix membrane

Zeolite loading	Permeability (Barrer *)		Selectivity CO_2/CH_4
	CO_2	CH_4	
Neat	6.54 ± 0.15	0.19 ± 0.01	33.59
10 wt%	3.41 ± 0.08	0.14 ± 0.01	24.35
25 wt%	5.02 ± 0.23	0.11 ± 0.05	46.05
40 wt%	6.13 ± 0.02	0.14 ± 0.02	43.17
50 wt%	8.59 ± 0.13	0.28 ± 0.01	30.86

* Barrer = 1 x 10^{-10} cm^3 (STP) cm/cm^2 s cmHg
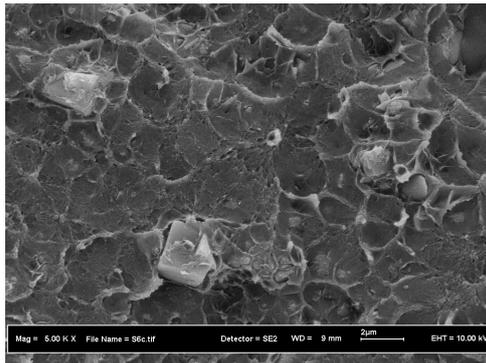
Figure 4: Surface images of PI/PES-zeolites 4A mixed matrix membranes with 25 wt% zeolite loading
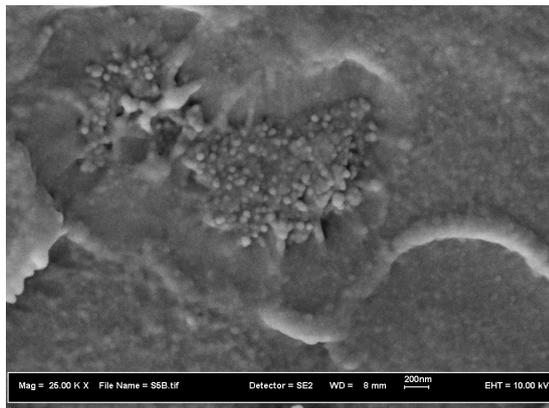
Figure 5: Surface images of PI/PES-zeolites 4A mixed matrix membranes with 40 wt% zeolite loading

As presented in Table 2, the trend of permeability of PI/PES mixed matrix membrane as a function of zeolite loading was similar for all of the gases studied. It indicated that there was a similar permeation mechanism for all of the membranes. The increase in permeability with increasing zeolite loading in the polymer matrix might be due to the disruption of polymer chain packing in the presence of zeolite particle which could increase the free volume available for molecular transport. The unselective voids in the interface of zeolite particle and polymer matrix might be formed due to high zeolite loading in mixed matrix membrane. Thus, the resistance to flow through zeolite particles were significantly reduced. The FESEM in Figures 5-6 supported that not all zeolite particles were well-distributed through the matrix and some of the zeolite particles formed small domains when the zeolite loading is as high as 50 wt%. Therefore, the zeolite loading was limited to equal or below 40 wt% for the gas permeation test. From Table 2, it can be concluded that the optimum loading of the zeolite was 25 wt% where the selectivity of the gas were at the highest values.
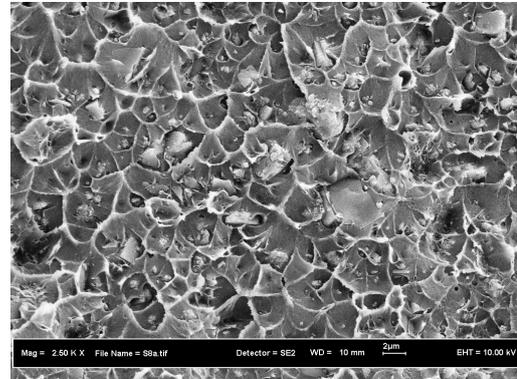
Figure 6: Surface images of PI/PES-zeolite 4A mixed matrix membranes with 50 wt% zeolite loading

IV. CONCLUSION

In this paper confirmed that the PI/PES-zeolite 4A with 25 wt % zeolite loading together with the 25 wt% polymer concentration showed the best performance in terms of gas permeability and selectivity for CO_2/CH_4 gas. In this study was also observed that the zeolite loading was significantly affected the gas separation performance of PI/PES-zeolite hybrid mixed matrix membrane. The FESEM images show that the dope should be prepared with sufficiently high polymer concentration and further heat treated at an appropriate temperature close to Tg to form a good contact between zeolite particles and polymer matrix. The unselective voids in the interface of polymer matrix with inorganic filler such as zeolite might be formed due to high zeolite loading in hybrid mixed matrix membrane.

REFERENCES

[1] Suer, M.G., Bac, N. and Yilmaz. L. 1994. Gas Permeation Characteristics of Polymer-Zeolite Mixed Matrix Membranes, Journal of Membrane Science, 91: 77-86.

[2] Duval, J.-M., Folkers, B., Kemperman, A.J.B., Mulder, M.H.V., Desgrandchamps, G. and Smolders, C.A. 1994. Adsorbent-filled Membranes for Gas Separation. Part 1. Improvement of the Gas Separation Properties of Polymeric Mem¬branes by Incorporation of Microporous Adsorbents. Journal of Membrane Science, 80: 189-198.

[3] Zimmerman, C.M., A. Singh, and W.J. Koros. 1997. Tailoring Mixed Matrix Composite Membranes for Gas Separations. Journal of Membrane Science, 137:145-154.

[4] Vankelecom, I.F.J. Van den Broeck, S. Merckx, E. Geerts, H. Grobet, P. Uytterhoeven, J.B. 1996. Silylation to improve incorporation of zeolites in

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Polyimides Films, Journal of Physical Chemistry, 100: 3753-3758.

[5] Ismail, A.F., T.D. Kusworo, A. Mustafa, 2008. Enhanced gas permeation performance of polyethersulfone mixed matrix hollow fiber membranes using novel Dynasylan Ameo silane agent, Journal of Membrane Science 319: 306-312.

[6] Kusworo, T.D., A.F. Ismail, A. Mustafa and T. Matsuura, 2008. Dependence of Membrane Morphology and Performance on Preparation Conditions: The Shear Rate Effect in Membrane Casting, Separation and Purification Technology, 61: 249-257.

[7] Mahajan, R. Koros, W.J. (2000). Factors Controlling Successful Formation of Mixed-Matrix Gas Separation Materials, Industrial Engineering and Chemical Resources. 39: 2692–2696