Effects of Silica Loading on the Absorption of Carbon Dioxide by Mixed Matrix Membranes

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ABSTRACT: *Fumed silica nanoparticles, TS-530 were used with polyvinylidene fluoride (PVDF) in this work to produce mixed matrix membranes (MMM). Various nanoparticle loading were used to observe the effects of different nanoparticle loading on the characteristics, morphology and gas absorption performance of the resulting MMMs. 0.5 wt%, 1.0 wt%, 1.5 wt%, 3 wt%, 5 wt% and 10 wt% silica nanoparticles were added into the polymer dope solution before the membranes were cast in flat sheet configuration. Membrane contact angle tests showed an increase of the contact angle with silica loading, which is a desired characteristic in membrane gas absorption process. Energy dispersive X-ray (EDX) surface mapping of these MMMs indicated that the nanoparticles were quite well distributed in the polymer matrix despite its tendency to agglomerate. Permeability of carbon dioxide (CO_2) in a gas mixture of CO_2 and nitrogen (N_2) for MMMs were better compared to the pure PVDF membrane, with 1 wt% silica loading having the best CO_2 permeability. Selectivity, however, decreased with increasing nanoparticles loading, which may be the result of poor compatibility between the nanoparticles and the polymer matrix.*

Keywords: Mixed matrix membrane, CO_2 absorption, membrane gas absorption, silica loading, polyvinylidene

1. INTRODUCTION

A method proposed to reduce the emission of greenhouse gases is carbon capture and storage (CCS) system. Membrane gas absorption (MGA) is an attractive alternative to the conventional chemical absorption systems. Of the commonly used hydrophobic polymers, polyvinylidene fluoride (PVDF) is the most attractive

due to its processability.[1] Mixed matrix membranes (MMMs) have the potential to show better performance by combining the desired characteristics of polymer and inorganic membranes.[2] Research has found that MMMs incorporating non-porous inorganic particles do not perform as predicted by the Maxwell model, which assumed decreased gas permeabilities in MMM compared to pure polymeric membranes.[3] The increase in free volume from the addition of non-porous silica nanoparticles causes an increase of gas permeability with silica content; however, the selectivity can decrease.[3,4] However, the incorporation of fumed silica nanoparticles in glassy polymers enhanced the gas and vapour permeability as well as the reverse selectivity for condensable C3+ hydrocarbons over smaller gases.[5] In the present study, silica nanoparticles at different loadings were added into PVDF, and the effects on the characteristics and performance of the resulting MMMs were investigated. The performance of the MMM in a MGA process to absorb CO_2 from flue gas were observed and compared with the pure PVDF membrane.

2.   EXPERIMENTAL

2.1   Materials

PVDF from Solef Company (Solef 6010/1001) was used as the polymer to synthesise the membranes. N-Methyl-2-pyrrolidone (NMP) from Sigma-Aldrich was used as a solvent. Hydrophobic fumed silica nanoparticles, Cabosil TS-530 containing trimethylsilyl groups was kindly supplied by Cabot Corporation (Tuscola, IL, United States).

2.2   Membrane Preparation

To synthesise MMMs, the desired amount of fumed silica nanoparticles were added into the solvent and stirred for 30 min. A range of nanoparticle loading of 0.5 wt% to 10 wt% was chosen as the addition of inorganic fillers beyond this amount would cause the particles to agglomerate too much. The mixture was then sonicated for 30 min to ensure that the nanoparticles were well dispersed within the solution. The PVDF powder was slowly added and then stirred continuously at 60°C for 24 h. The pure PVDF membrane was prepared in a similar manner, without the addition of the silica nanoparticles. The dope polymer solutions were cast by a casting machine (Elcometer 4340, United Kingdom) on a glass plate using a casting blade to set a thickness gap of 400 μm. The cast polymer solution was immediately immersed into a coagulation bath containing 20 wt% ethanol in water for 24 h. Then, the membrane film was thoroughly washed with water to remove the excess chemicals.

2.3　Characterisation

The water contact angle of the MMMs was measured using a goniometer (Ramé-Hart Instruments Co.). The pore size distribution of the membranes was obtained by wetting the membrane samples with Porefil for 10 min before using a porometer, Porolux 1000 (Beneflux Scientific, Belgium) with N_2 gas. The thermal degradation of membranes was observed in inert N_2 through a thermal gravimetric analysis (TGA). The liquid entry pressure of the membranes (LEP_w) was measured by a porometer using the bubble point method.[6] The morphology of the membranes was observed using field emission scanning electron microscope (FESEM, SUPRA TM 35vp Zeiss, Germany). EDX surface mapping for the top surface of the MMMs was done to observe the dispersion of silica nanoparticles on the surface of the MMMs.

2.4　Gas Absorption Test

Membrane sample with a diameter of 19 mm was placed in the membrane module. Pure CO_2 and N_2 gases at 100 ml min^{-1} were used as feed gas while distilled water at 100 ml min^{-1} was used as the liquid absorbent in the MGA system. The liquid absorbent from the outlet was collected to measure the absorbed CO_2 from the gas stream using chemical titration method.[7] The CO_2 flux through the membrane can be determined using Equation 1:[1]

$$CO_{2_{flux}} = \frac{C_{CO_2} \times Q_{absorbent}}{A} \qquad (1)$$

where C_{CO_2} is the concentration of absorbed CO_2, $Q_{absorbent}$ is the absorbent flow rate (l/s) and A is the effective membrane surface area (m^2).

3.　RESULTS AND DISCUSSION

3.1　Membrane Characterisation

In MGA process, it is desirable for the membrane to be hydrophobic to avoid membrane wetting, which causes the membrane performance to deteriorate. The characterisation results of synthesised membranes are shown in Table 1. The addition of the hydrophobic silica nanoparticles to the already hydrophobic PVDF polymer initially showed a decrease in water contact angle. However, with the addition of more silica nanoparticles, the water contact angle of the MMMs showed a steady increase, which could increase the membrane sustainability in

the long run. LEP_w depends on the wettability, connectivity and surface pore size of the membrane.[6] The increasing LEP_w of the MMMs with silica loading was related to the presence of the hydrophobic modified silica nanoparticles. From the TGA analysis, it was found that the pure PVDF membrane began to lose weight at approximately 188°C, but the presence of silica nanoparticles increased this value. The temperatures at 1% (T_1) and 5% (T_5) weight loss increased with silica loading, proving that the addition of fumed silica nanoparticles enhanced the thermal stability of the MMMs.[8]

Table 1: Characterisation results of synthesised membranes.

Membrane	Pore size (µm)	LEPw (bar)	Porosity (%)	Contact angle (°)
Pure PVDF	0.12	4.747	76.77	90.7
0.5% TS-530	0.10	7.424	75.86	84.3
1% TS-530	0.08	7.511	77.57	91.4
1.5% TS-530	0.09	7.567	78.50	95.6
3% TS-530	0.09	7.618	77.46	99.1
5% TS-530	0.10	7.841	72.70	108.5
10% TS-530	0.11	7.870	66.51	110.7

Figure 1 shows the morphology of the pure PVDF membrane and MMMs obtained from the FESEM analysis. The morphologies of the membranes were similar, but MMMs with 3 wt%, 5 wt% and 10 wt% particles loading had visibly denser sponge-like bottom layers, and this was further confirmed by the porosity of the membranes, which decreased after the 1.5 wt% silica loading. MMMs had lower thickness compared to the pure membrane due to the alteration of PVDF chain packing with addition of nanoparticles. The EDX results show that the fumed silica nanoparticles were well-distributed on the surface of the MMMs. This is attributed to the hydrophobic nature of the modified silica nanoparticles. The average pore radius of the MMMs decreased when 1 wt% silica was used, then increased with silica loading. The large pore sizes of the pure PVDF membrane can be attributed to the large finger-like layer. In the phase-inversion process, the thermodynamic and kinetic effects determined the structure of the membrane. Contrary to the effects of addition of PEG-400 in the dope solution by Mansourizadeh and Pouranfard, the addition of fumed silica nanoparticles into the dope solution had possibly increased the thermodynamic miscibility of the solution, which discouraged liquid-liquid phase separation and formed membranes with lower porosity.[9] Furthermore, the addition of inorganic fillers increased dope solution viscosity, delaying the diffusion during the phase separation. This delay could suppress the growth of the finger-like layer, producing membranes with lower pore volume smaller finger-likes.
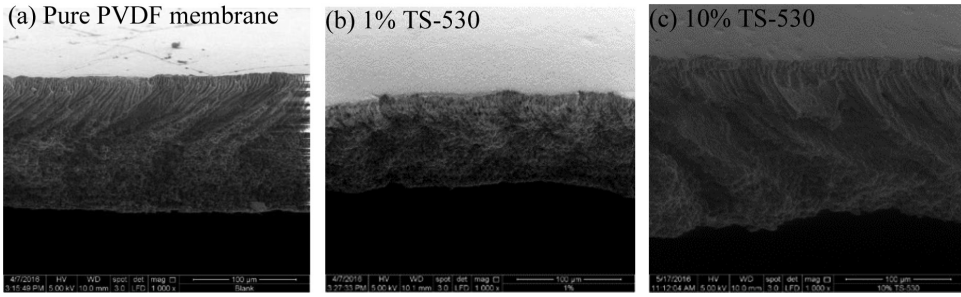
Figure 1:   FESEM images of the cross-sectional view of (a) pure PVDF membrane and MMMs containing (b) 1% and (c) 10% TS-530 fumed silica nanoparticles.

3.2   Membrane Absorption Test

Figure 2 shows the CO_2 absorption flux and CO_2/N_2 selectivity of the synthesised MMMs. The highest absorption flux achieved by the synthesised MMMs was at 1.5 wt% silica loading with 2.82×10^{-4} mol m^{-2} s^{-1} while the highest CO_2/N_2 selectivity was at 1 wt% silica loading with 22.5. Comparing these CO_2 fluxes and selectivity with the ones obtained by the pure PVDF membrane (2.84×10^{-4} mol m^{-2} s^{-1} and 7.18, respectively), it can be seen that while the MMMs did not manage to surpass the pure PVDF membrane in terms of CO_2 flux, its selectivity increased significantly. The large pore size of the pure PVDF membrane was the reason for the high CO_2 and N_2 flux, causing its selectivity to decrease. On the other hand, 1 wt% MMM had smaller pore size which accounted for the significant increase in selectivity, but the narrow gaps between silica-polymer interface allowed the CO_2 to diffuse through the membrane. Higher silica loadings led to larger agglomeration
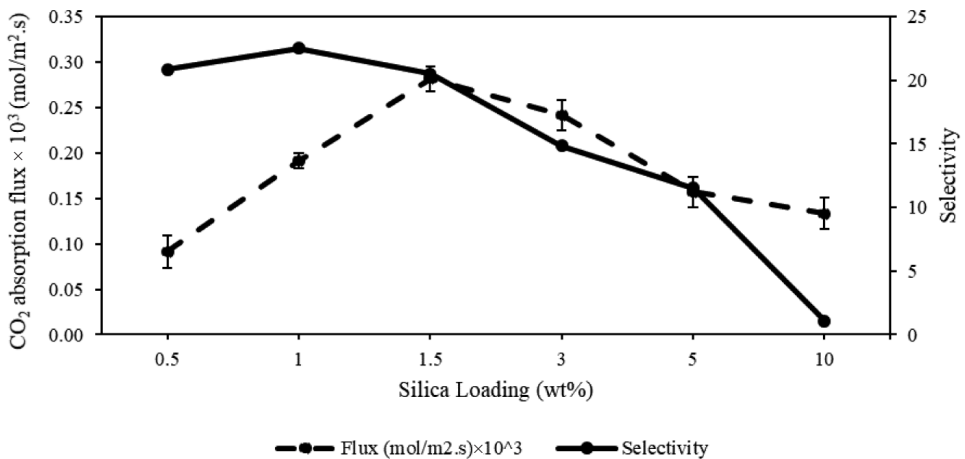

Figure 2: CO_2 flux and selectivity of MMMs with silica loading.

of the inorganic fillers, forming more non-selective voids, which was why the CO_2/N_2 selectivity decreased.[10] The decrease in CO_2 permeability with higher silica loading can be attributed to the decrease in porosity of the MMMs, as well as the significant change in the polymer chain packing, causing the gas diffusion path to become longer and more tortuous.[1]

4.   CONCLUSION

Hydrophobic PVDF mixed matrix membranes incorporated with non-porous fumed silica nanoparticles were synthesised in this work. The presence of these hydrophobic nanoparticles gave rise to the water contact angle and liquid entry pressure of the MMMs, while decreasing their porosity. The increase in inorganic fillers reduced the depth of finger-like layer of the MMMs and caused the sponge-like layer to become more dense, even as the average surface pore size to increase as a result of the formation of large silica aggregates. In the gas absorption test using an MGA system, the MMM containing 1.5% silica loading had the highest CO_2 absorption flux among the MMMs while the MMM with 1% silica loading had the highest CO_2/N_2 selectivity which is almost three times the selectivity of the pure PVDF membrane.

5.   ACKNOWLEDGEMENTS

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