Solid-Liquid-Polymer Mixed Matrix Membrane Using Liquid Additive Adsorbed on Activated Carbon Dispersed in Polymeric Membrane for CO_2/CH_4 Separation

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Abstract—Gas separation by selective transport through polymeric membranes is one of the rapid growing branches of membrane technology. However, the tradeoff between the permeability and selectivity is one of the critical challenges encountered by pure polymer membranes, which in turn limits their large-scale application. To enhance gas separation performances, mixed matrix membranes (MMMs) have been developed. In this study, MMMs were prepared by a solution-coating method and tested for CO_2/CH_4 separation through permeability and selectivity using a membrane testing unit at room temperature and a pressure of 100 psig. The fabricated MMMs were composed of silicone rubber dispersed with the activated carbon individually absorbed with polyethylene glycol (PEG) as a liquid additive. PEG emulsified silicone rubber MMMs showed superior gas separation on cellulose acetate membrane with both high permeability and selectivity compared with silicone rubber membrane and alone support membrane. However, the MMMs performed limited stability resulting from the undesirable PEG leakage. To stabilize the MMMs, PEG was then incorporated into activated carbon by adsorption. It was found that the incorporation of solid and liquid was effective to improve the separation performance of MMMs.

Keywords—Mixed matrix membrane, membrane, CO_2/CH_4 separation, activated carbon.

I. Introduction

MEMBRANE technology for gas separation processes has encountered a great development since the first type of membrane-based industrial gas separation process was introduced about 20 years ago. It has been used in a wide range of applications, and the number of applications is still growing [1], [2].

A membrane can be defined as a selective barrier between two sides of gas mixture, and the term "selective" is inherent to a membrane or a membrane process. The membrane gas separation technology is demonstrating as one of the most important unit operations. The membrane technology provides many advantages over other methods including compactness and light weight, low labor harshness, modular design that allows for facile enlargement or operation at partial capacity, low maintenance, low energy consumptions, low capital cost, and environmentally friendly operations [3]. A schematic representation of a simple gas separation membrane process is shown in Fig. 1. A pressurized feed stream containing A and B comes in contact with the membrane surface. The membrane helps to produce a permeate containing pure A and a retentate containing pure B.
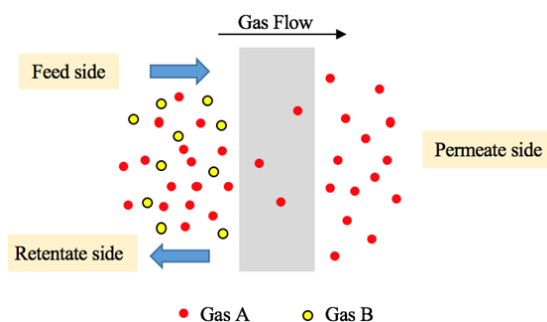

Fig. 1 Schematic representation of membrane separation

Polymeric membranes which are one of the most important divisions of membranes preferentially in gas separation have a proprietary of many desired properties including low capital investment, low energy consumption, high specific surface area per module, and easy processing. However, these polymeric membranes undergo low operating temperature and tradeoff between their permeabilities and selectivities and cannot be operated under severe conditions. Therefore, pure polymeric membranes have been faced with low tradeoff which immensely limits their economical applications in the chemical and petrochemical industries [4], [18].

To enhance the commercial applicability of membrane technology, MMMs have been developed by adding molecular sieving material such as zeolites and non-zeolite particles through incorporating these sieves into polymeric phase. An alternative approach is to design membranes that combine the best characteristics of both polymeric and porous materials, by forming organic-inorganic hybrid membranes [5]. The ultimate aim is to get desired combination of the properties for better gas separation, i.e. high permeability, selectivity, physical stability, and low energy requirement, ease of operation, and finally low capital and operational cost.

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II. CONCEPT OF MMMs

Polymeric membranes designed for gas separations have been known to have a trade-off between permeability and selectivity under Robeson's upper bound [6], [10]. Attempts at merely altering the chemical structure of the polymer offered diminishing returns in improving performance [7].

In 1999, theoretical work by Freeman concluded that there is an asymptotic limit to the separation capabilities of polymeric membranes [15]. This work aimed at developing membranes capable of operating above the upper bound has focused on MMMs. These membranes combine polymer with an inorganic filler, usually a zeolite or a molecular sieve. Although inorganic molecular sieves lie well above the Robeson's upper bound or near the commercially attractive region. These materials are expensive and difficult to process and handle as membranes, brittle and difficult to upscale [5].

MMMs with hybrid characteristics of polymer and inorganic materials, were developed as an alternative approach to overcome these limitations. MMMs or hybrid membranes are considered as a class of composite membranes that comprise of inorganic materials embedded in a polymer matrix. Fig. 2 shows the schematic diagram of a MMM.
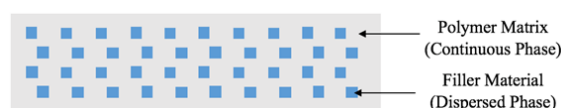

Fig. 2 Schematic representation of a MMM

Generally, the inorganic dispersed phase has selectivity superior to the neat polymer. Hybrid membranes have transport properties in between the pure polymer and the dispersed phases. Ideally, the incorporation of small fractions of inorganic fillers into the polymer matrix can result in a significant improvement in the overall performance.

For solid-liquid-polymer MMM, it has been developed to avoid undesirable liquid leakage from polymer by using liquid additive absorbed in pores of porous materials and then dispersed into polymer phase [11].

III. EXPERIMENTAL

A. Materials

Silicone rubber as continuous polymer phase used in this work was RTV615A and a curing agent RTV615B from General Electric Co., Ltd. Liquid additive, PEG MW400, and activated carbon (AC) were obtained from Aldrich Chemical, Inc. Cellulose acetate (CA) support membranes casted on non-woven cloth were obtained from UOP. The solvent used was hexane from Aldrich Chemical, Inc. The gases used included carbon dioxide (CO_2), methane (CH_4), and nitrogen (N_2) with their physical properties which are shown in Table I.

B. Membrane Preparation

PEG-activated carbon-silicone rubber MMMs were prepared by solution-coating and solvent evaporation methods as schematically presented in Fig. 3. The solution was formed by mixing RTV615A silicone rubber with RTV615B curing agent in hexane. In the meantime, liquid was separately mixed with hexane. The liquid solution was then admixed into the RTV solution followed by activated carbon. After mixing together, the obtained solution was then coated on a support membrane. The coated membrane was allowed to cure in an oven at a temperature of 85 °C for 2h to initiate the crosslinking reaction and to remove the residue solvent.

TABLE I
PHYSICAL PROPERTIES OF GASES CO_2, N_2 AND CH_4 (RATON, 2004)

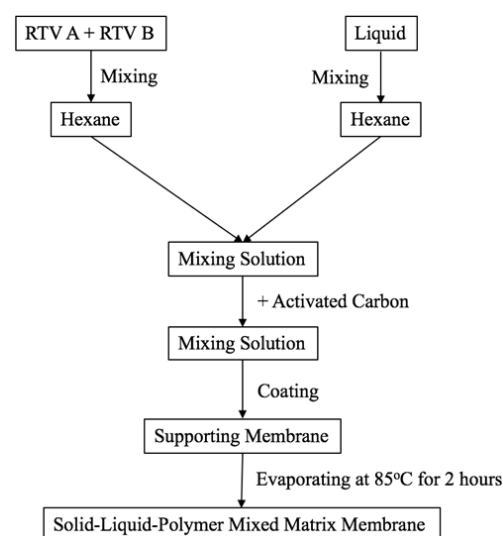| Gas	Molecular mass (g/mol)	Critical temperature (K)	Kinetic diameter (nm)
CO_2	44	304	0.33
N_2	28	126	0.36
CH_4	16	190	0.38

Fig. 3 Flow diagram of the solid-liquid-polymer membrane preparation procedure

C. Gas Permeance Measurements

The experimental setup used for the determination of gas permeability is schematically shown in Fig. 4. A membrane sample of 7.5 cm in diameter was placed inside a membrane testing unit with an O-ring forming a seal around the edge. The membrane was supported by a porous metal plate. The testing unit was pressurized with a single gas at 100 psig at the feed side. After a time-interval estimated to be sufficient for attaining steady state, flux of gas was measured using a bubble flow meter. Before applying another gas, the membrane was purged with N_2 to get rid of the residual gas.

IV. RESULTS AND DISCUSSION

Permeance (P_A/L) is determined from steady-state permeation rates of CO_2, CH_4, and N_2 through the membranes. The permeation rate measurements were made with all gases at room temperature, and its permeances were calculated using (1). The experimental results are presented in Table II.

$$P_A/L = J_A/\Delta p_A \qquad (1)$$

where P_A/L is the gas permeance in GPU unit. J_A is the penetrant diffusive flux through the membrane, and Δp_A is the change in partial pressure across the membrane (cmHg).
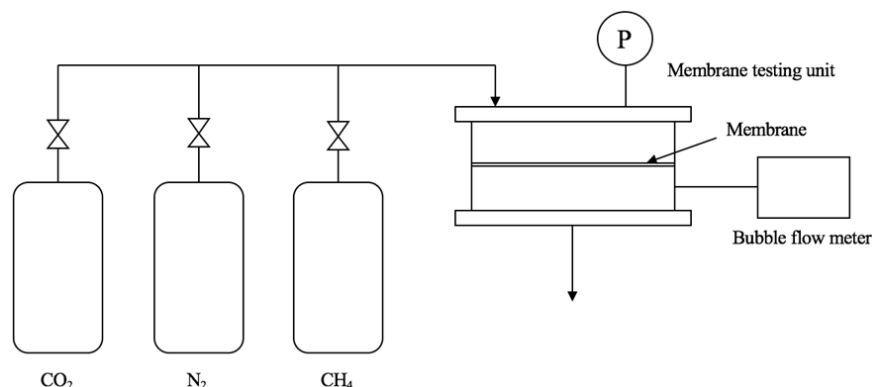

Fig. 4 Schematic of the experimental setup for measuring gas permeability

TABLE II
GAS PERMEANCE AND SELECTIVITY FOR THE FABRICATED MEMBRANE

Membrane	Gas Permeance (GPU[a])			Selectivity (P_{CO2}/P_{CH4})
	CO_2	CH_4	N_2	
CA	16357	28458	19647	0.58
SR/CA	206.50	40.60	20.30	5.09
5PEG/SR/CA MMM	83.63	13.26	5.61	6.31
AC/SR/CA MMM	342.50	57.26	38.98	5.98
5PEG/AC/SR/CA MMM	114.82	9.25	5.25	12.42
10PEG/AC/SR/CA MMM	91.70	6.49	5.00	14.12
20PEG/AC/SR/CA MMM	78.13	5.98	4.47	13.07

[a]$GPU = 10^{-6} cm^3 (STP) \cdot cm^{-2} \cdot s^{-1} \cdot cmHg^{-1}$

It is seen that the values of permeance for the penetrant gases through cellulose acetate support membranes decrease in the following order: $CH_4 > N_2 > CO_2$. The support membrane exhibited no CO_2/CH_4 separation performance.

Silicone rubber is rubbery polymer, of which the segments of backbones can rotate freely around their axis; this makes the polymer soft and rubbery [8]. Transport of gas through rubbery polymer is postulated to occur when there is a transient gap of sufficient size to accommodate the penetrant. This transient gap forms and fades throughout the polymer matrix due to thermally induced motion of the polymer segments [9]. The membrane with coating silicone rubber (SR/CA) yields much lower gas permeances but a higher CO_2/CH_4 selectivity.

In comparison, with PEG/SR/CA MMM, it exhibits lower gas permeances than SR/CA. The added PEG filled up the transient gap between polymer chain and hindered the diffusion path of gas molecules. In this regard, gas molecule permeates slower. This may be believed that PEG normally being plasticizer not only has the capacity of altering the permeance of SR, but it also acts on the polymeric support material by softening it and causing its pore to shrink [12].

Membrane containing PEG shows a better separation performance than SR/CA due to the enhancement in gas selectivity. PEG enhances solubility coefficient of CO_2 by allowing CO_2 to pass through with a more rapid rate than membrane without PEG. It was found that the hydroxyl groups, which are presented in each of the PEG molecules, are the major determiner of solubility of CO_2 into a membrane. The O-H bond is strongly polar. This polarity induces the formation of London force arose from temporary dipole moment [16]. Thus, CO_2 molecules which are more polar than CH_4 molecules can pass through the polymer matrix by solubility.

In order to enhance the gas permeability and selectivity properties of polymeric membrane, the incorporation of solid component such as activated carbon (AC) was added into the matrix phase. The AC/SR/CA MMM exhibits higher permeance and CO_2/CH_4 selectivity than SR/CA membrane because the AC/SR/CA MMM has the capacity of altering selectivity of silicone rubber. The controlling mechanism which is involved in the selectivity enhancement is size selective such that smaller molecules (CO_2, kinetic diameter is 0.33 nm) permeate better than bigger molecules (CH_4, kinetic diameter is 0.38 nm) as shown in Fig. 5 [17].
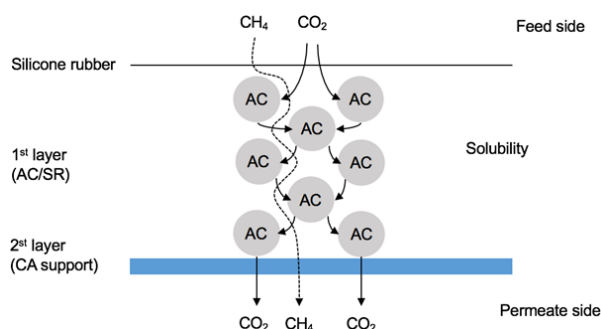

Fig. 5 Gas transport mechanism through AC/SR/CA MMM

It was found from a previous work that a PEG emulsified silicone rubber MMM, through its capability of altering selectivity of silicone rubber, lost its stability due to PEG leakage [13]. In this study, activated carbon was used to prevent such incident by being incorporated into PEG solution

prior to being added into the matrix phase. AC/SR/CA MMM exhibits higher permeance for both gases than the PEG/AC/SR/CA MMM due to the presence of PEG on the surface of AC which hindered the path of gas diffusion. In contrast, the selectivity of PEG/AC/SR/CA MMM is higher than AC/SR/CA MMM since CO_2 passes through the PEG/AC/SR/CA MMM with a more rapid rate due to the higher solubility of CO_2 in PEG and SR and more selective to CO_2 in AC compared with CH_4.

It is clearly seen from Table II that the incorporation of more amount of PEG into AC/SR/CA MMM results in the decreases of CO_2 and CH_4 permeance compared to AC/SR/CA MMM. Due to the dominance of PEG crystallinity [14], it caused denser intersegment packing and hindered the gas transport. However, the optimum CO_2/CH_4 selectivity could be attained as an appropriate amount of PEG was incorporated.

V. Conclusion

All MMMs were prepared by the solution-coating method and were tested for permeance and selectivity of CO_2/CH_4 at room temperature with single gas measurements. The selectivity of SR/CA membrane was significantly improved when added PEG into the matrix. In the case of AC/SR/CA MMM, the selectivity was also increased compared with SR/CA membrane. Besides, the higher selectivity was obtained by incorporating AC into the PEG/ SR/CA MMM to prevent the leak out of PEG from the surface of the membrane. The CO_2/CH_4 selectivity increased as the concentration of PEG in the membrane increased to the optimum loading. In addition, it was found that 10PEG/AC/SR/CA MMM provides the highest performance for CO_2/CH_4 separation.

Acknowledgment

References

[1] W. L. McCabe, J. C. Smith, P. Harriott (1993). "Membrane separation process". Unit Operation of Chemical Engineering. Singapore: McGraw-Hill.
[2] S. L. Matson, J. Lopez, J. A Quinn (1983). "Membrane Separation". Chemical Engineering Science, 38, 503.
[3] A. Basu, J. Akhtar, M. H. Rahman, M. R. Islam (2004). "A review of separartion of gases using membrane system". Petroleum Science Technology, 22, 1343.
[4] Y. Zhang, K. J. Balkus, I. H. Musselman, Ferraris, J. P. Ferraris (2008). "Mixed-matrix membranes composed of matrimid and mesoporous ZSM-5 nanoparticles". Journal of Membrane Science, 325, 28-39.
[5] S. Kulprathipanja (2010). "Zeolites in Industrial Separation and Catalysis". Weinheim: WILEY-VCH Verlag Gmbtt & CO.
[6] L. M Robeson. (1999). "Polymer membranes for gas separation, current opinion in solid state & materials". Science, 4, 549-552.
[7] Y. Zhang, J. Sunarso, S. Liu, R. Wang (2013). "Current status and development of membranes for CO2/CH4 separation; A review".
International Journal of Greenhouse Gas Control, 12, 84-107.
[8] W. J. Koros, G. K. Fleming, S. M. Jordan, Kim, T. H., Hoehn, H. H. (1988). "Polymeric membrane materials for solution-diffusion based permeation separations". Progress in Polymer Science, 12, 84-107.
[9] W. J. Koros, M. R. Coleman, D. R. B. Walker (1992). "Controlled permeability polymer membranes". Annual Review of Material Science, 22, 47-89.
[10] L. M. Robeson (2008). "The upper bound revisited". Journal of Membrane Science, 320, 390-400.
[11] S. Kulprathipanja (2002). "Reactive Separation Process". New York: Taylor & Francis.
[12] S. Kulprathipanja, S. S. Kulkani (1986). Separation of polar gases from non-polar gases. U.S. Patent 4 608 060.
[13] P. Vijitjunya (2001). "Dispersed liquid-polymer mixed matrix membrane for olefin/paraffin separation". M. S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University.
[14] N. N. Li, A. G. Fane, W. S. W. Ho, T. Matsuura (2008). "Advanced Membrane Technology and Applications". New Jersey: Wiley & Sons, Inc.
[15] B. D. Freeman (1999). "Basis of permeability/selectivity tradeoff relations in polymeric gas separation membranes". Macromolecules, 32, 375.
[16] V. Sirivalsatit (1999). "The mechanism of the mixed matrix membrane separation (polyethylene glycol/silicone rubber) for polar gases". M. S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University.
[17] A. Soffer, J. Gilron (1996). U.S. Patent 5 914 434.
[18] O. Bakhtiari, S. Mosleh, T. Khosravi, T. Mohammadi (2011). "Preparation, charaterization and gas permeation of polyimide mixed matrix membranes". Membrane Science & Technology, 1:101.