Applied Mechanics and Materials Vol. 625 (2014) pp 690-695
© (2014) Trans Tech Publications, Switzerland
doi:10.4028/www.scientific.net/AMM.625.690

Polymer-Nanoclay Mixed Matrix Membranes for CO_2/CH_4 Separation: A Review

Asif Jamil [a] *, Oh Pei Ching [b] and Azmi B M Shariff [c]

Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Perak, Malaysia

[a]asif.jamil8@gmail.com, [b]peiching.oh@petronas.com.my, [c]azmish@petronas.com.my

Keywords: Mixed matrix membranes, montmorillonite, nanoclay, CO_2/CH_4 separation

Abstract. Mixed matrix membrane (MMM) has shown significant progress towards gas separation. Rigid polymers are suitable materials for MMM fabrication but adhesion problems with filler need to be addressed. A variety of inorganic fillers have been studied for CO_2 separation but clay minerals were not considered much in this class. The layered silicate structure of nanoclay such as montmorillonite provides excellent opportunity to manipulate its properties, leading towards better dispersion and adhesion towards the polymer matrix. This paper reviews the potential of polymer-nanoclay MMM for CO_2/CH_4 separation.

Introduction

In recent years, efforts are underway to improve separation processes via membrane technology due to its versatility in gas separation, ease of processing, low capital and operational cost, small footprint and energy efficiency [1]. In 1991, Robeson proposed the upper bound limit which shows the trade-off between permeability and selectivity for membrane materials. According to the curve, polymeric materials exist far below the upper bound limit whereas inorganic materials resided in the upper bound region [2]. Tremendous improvement has been shown by polymeric membranes over the past decade but a fine balance between permeance and selectivity is yet to be achieved; whereas inorganic membranes are superior in terms of selectivity but its low processing ability, brittleness and higher capital cost bounds its commercial application. The notion behind mixed matrix membrane (MMM) was to combine the permeance of polymeric material and selectivity of inorganic material to create a state-of-the-art hybrid membrane. MMM is comprised of a polymer phase dispersed with inorganic filler. On a commercial scale, polymers like Udel, Matrimid and Ultem are commonly used for incorporation of heterogeneous phase to improve gas separation properties [3, 4]. Rigid polymers with high T_g, seems appropriate in achieving upper bound performance but its weak adhesion towards inorganic filler oppose the eminent formation of the membrane [5-7].

MMM incorporating Inorganic Fillers

Inorganic fillers embedded in a polymer matrix have potentials to enhance the polymer matrix selectivity. Generally, there are two types of inorganic fillers: porous and non-porous. Carbon molecular sieve (CMS), carbon nanotube (CNT) and zeolite are examples of porous fillers, where transportation of molecules occurs through diffusion process. On the contrary, transportation of molecules for non-porous inorganic fillers such as nanoclay, silica and metal-organic framework (MOF) is based on solubility selectivity [1, 8-11].

Zeolites are widely used as porous nanofillers in MMM for CO_2/CH_4 separation. A 50% increment in membrane selectivity as compared to neat polymer membrane is observed by the addition of zeolite in selective skin layers of PSf/Matrimid hollow fibre membrane [12]. Similarly, by incorporating CMS in Matrimid and Ultem, the selectivity enhancement for CO_2/CH_4 gas was approximately 45% and 40% respectively, as compared to neat polymers [13]. Non-porous fillers disrupt the chain packing in rigid polymers, increase the free volume, and ultimately give higher permeability. Nevertheless, void formation at the surface of nanofillers due to poor adhesion with polymer matrix might also result in permeability enhancement. In a study, hydrated silica, a type of non-porous inorganic filler is incorporated in polybenzimidazole (PBI) matrix. Solubility rise for condensable gases is observed due to the existence of OH groups in the polymer matrix. As diffusion permeation mechanism is responsible for gas transportation in neat PBI membrane contrary to hybrid membrane where solution mechanism prevails, this resulted in decreased permeation for non-condensable gases, which subsequently leads to gas separation in the existence of silica particles [14]. Another type of non-porous inorganic filler, namely clay mineral, has yet to receive much attention in MMM development for gas separation applications although it is prominently used in polymer composite industry [15]. It is found that even at low clay loading (≤10 mass % clay); there is enhancement in thermal, mechanical, optical, electrical, flammability and barrier properties [16-20]. Table 1 compares the transport properties of various porous and non-porous inorganic fillers in different polymer matrix. The change in permeance and selectivity values are reported in comparison to neat polymer.

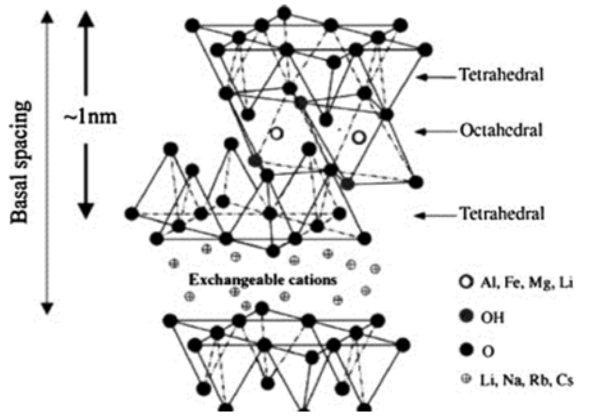

Figure 1: General structure of montmorillonite [15].

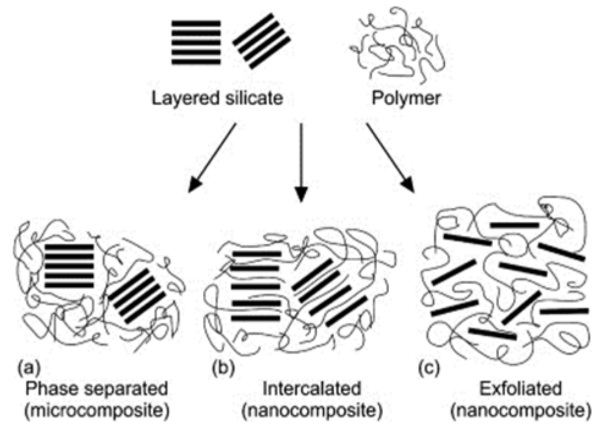

Figure 2: Possible distribution of layered silicates in polymer matrix [11].

Clay Minerals

Clay minerals are cheap, green materials that are abundantly available. Structurally, they exist in layers of aluminosilicates that are built up of crystalline aluminium tetrahedral sandwiched between silica layers. These layers are bonded by weak electrostatic and Van der Waal forces [15]. Clay minerals can be subdivided into five different groups such as smectite, illite, kaolinite, chlorite or sepiolite. Montmorillonite (MMT), a member of the smectite family, is extensively used as clay filler. It consists of two tetrahedral fused sheets sandwiching an edge shared octahedral sheet of aluminium, as shown in Fig. 1 [11, 21]. Due to the electronegative nature of the layers, the spacing in between these layers is generally occupied by cations such as Li^+, Na^+, Rb^+, and Cs^+ [15, 16]. MMT clays tend to attract water between layers due to their hydrophilic nature. This resulted in MMT having high cationic exchange capacity, thus MMT clays show promise as inorganic fillers for MMM development [22].

The addition of clay mineral in polymer matrix produces three different types of dispersion: phase separated, intercalated or exfoliated, depending on the interaction between the polymer and nanoclay as shown in Fig. 2 [11]. These morphologies offer significant improvement in mechanical, thermal and barrier properties of polymer-nanoclay hybrid materials [15]. In essence, the layered silicate obstructs diffusion pathways, reduces free volume in polymer systems, hence affect the sorption of more condensable gases [11, 23-25].

Table 1: Transport properties of porous and non-porous fillers in different polymer matrix.

Polymer	Nanofiller	Pressure (bar)	Temperature (^oC)	Permeability change (*p*) (%)	Selectivity change (*α*) (%)	Ref.
PSf	Fumed silica	4.4	35	140	-40	[15]
Psf	SWCNTs	4	35	31	-20	[15]
Matrimid 5218	CMS	3.4	35	26	45	[12, 13]
Psf/Matrimid	Zeolite beta	5	35	-20	50	[12]
Polymer-nanoclay hybrid Membranes						
PEI	Cloisite®15A	15	25	24	28	[22]
PSf	Cloisite®15A	5	25	270	-9.5	[15]
PEI	HNT	15	25	27	8	[26]
PDMS	Sepiolite	13.8	-	-	144	[27]
PDMS	TMA-MMT	13.8	-	-	91	[27]

Polymer-nanoclay mixed matrix membranes for CO_2/CH_4 Separation

In a recent study, Defontaine and colleagues incorporated clay minerals like sepiolite and tetramethylammonium intercalated montmorillonite (TMA-MMT) in polydimethylsiloxane (PDMS) matrix and observed tremendous increase in selectivity for CO_2/CH_4. In both cases, the silanol groups form covalent bonds between the clay minerals and growing polymer chains. By incorporating sepiolite as the nanofiller in PDMS matrix, silicate layers are covalently bonded with the polymer chain by Si-O-Si bonding due to abundantly present silanol groups at the external surfaces, which leads to drastic improvement of up to 144% in CO_2/CH_4 selectivity. On the other hand, due to the lower density of edged silanol groups in MMT, an increment of 91% in CO_2/CH_4 selectivity is achieved for TMA-MMT/PDMS MMMs under the same conditions compared to neat PDMS membranes [27].

In the work of Hashemifard, halloysite nanotube (HNT), also a member of the clay family is modified with N-β-(aminoethyl)-γ-aminopropyltrimethoxysilane (AEAPTMS) molecules to improve dispersion in polyetherimide (PEI) and create better adhesion between the organic and inorganic phases in MMM. It was observed that selectivity decreased for HNT/PEI MMM initially but optimizing the sonication and priming protocol leads to better dispersion. His work also revealed that increased silane concentration coupled with higher degree of tortuosity yielded higher selectivity in comparison to neat PEI membrane. Also, the presence of amine groups in the modified HNT/PEI MMM is effective in enhancing CO_2 adsorption, giving better permeability and selectivity for CO_2. According to his findings, 0.5% loading of silylated HNT yielded the optimum MMM in terms of CO_2 permeability and CO_2/CH_4 selectivity, showing an increase of 27% and 8%, respectively in comparison to neat PEI membrane [26].

In another study, Hashemifard demonstrated interesting results for CO_2/CH_4 separation in terms of permeability and selectivity when polyetherimide (PEI) matrix was embedded with raw and industrially modified montmorillonite nanoclay. Among the studied MMT, Cloisite® 15A which was intercalated by dimethyl, dehydrogenated tallow, quaternary ammonium provided better adhesion between the clay and PEI matrix, thus hindered void formation and resulted in better separation properties. The presence of tallow in clay gallery leads to improved adhesion whereas high aspect ratio of MMT leads to higher degree of tortuosity across the dense skin layer, which ultimately increases the selectivity up to 28% as compared to neat polymer. The optimum selectivity was obtained at 0.5% Cloisite® 15A loading. Increasing Cloisite® 15A loading beyond this limit resulted in decline in selectivity and permeability due to clay agglomeration and void formation [22].

A further example using industrially modified Cloisite® 15A was carried out by Zulhairun who fabricated asymmetric MMM using Polysulfone (PSf) as the polymer matrix. An astounding finding is that at low loading of Cloisite® 15A, CO_2 permeance showed more than 270% enhancement, with almost no effect on CO_2/CH_4 selectivity compared to that of neat PSf. These results are contrary to the concept that incorporation of clay filler resulted in permeability decrease. The author speculates that this depends on how clay layers are dispersed in the polymer matrix. High permeance might be due to non-intercalated or phase separated clay tactoids. The unexfoliated clay layers produced high perturbation in the polymer chains packing, leading to increased permeance. There might also be nano meter gaps around the inorganic phase and possibility of Knudsen diffusion through clay galleries and polymer clay interface. The barrier properties of the inorganic filler could be capitalised to enhance the selectivity of small condensable gas from the mixture containing non condensable large gases by increasing the path length for diffusion of large gases across MMM [15].

To date, less attention has been devoted to polymer-nanoclay mixed matrix membranes, yet initial findings ascertained the versatility of nanoclay as suitable inorganic nanofiller for CO_2/CH_4 separation.

Conclusion

At present, the existing polymeric membrane materials are incapable to meet most industrial requirements for gas separation, in terms of permeability and selectivity. Mixed matrix membranes benefit from the synergistic advantages of the desirable processing properties of polymeric materials coupled with the gas separation abilities of nanofillers. In previous years, various porous and non-porous nanofillers have been examined for gas separation applications. Non-porous fillers have been identified to change the chain packing of polymers and modify the gas separation ability of the polymer matrix. Among the non-porous fillers, clay minerals exhibit promising ability to vary polymer chain orientation. Like all other nanofillers, nanoclay dispersion states and void formation tendency in polymer matrix are the major challenges that require further study for future advancement in this area. The selection of the most suitable polymer matrix along with nano structured clay is needed of the hour. In future, membrane scientists need to discover new materials to functionalise the nanofiller surfaces which may pave the way towards better dispersion and adhesion.

Acknowledgement

This work was supported by Universiti Teknologi PETRONAS (UTP) and Ministry of Higher Education (MOHE), Malaysia under STIRF Grant No. 27/2012 and MyRA Research Grant.

References

[1] T.-S. Chung, L. Y. Jiang, Y. Li, and S. Kulprathipanja, "Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation," *Progress in Polymer Science,* vol. 32, pp. 483-507, 2007.

[2] L. M. Robeson, "Polymer membranes for gas separation," *Current Opinion in Solid State and Materials Science,* vol. 4, pp. 549-552, 1999.

[3] C. M. Zimmerman, A. Singh, and W. J. Koros, "Tailoring mixed matrix composite membranes for gas separations," *Journal of Membrane Science,* vol. 137, pp. 145-154, 1997.

[4] H. Lin and B. D. Freeman, "Materials selection guidelines for membranes that remove CO2 from gas mixtures," *Journal of Molecular Structure,* vol. 739, pp. 57-74, 2005.

[5] J. M. Duval, A. J. B. Kemperman, B. Folkers, M. H. V. Mulder, G. Desgrandchamps, and C. A. Smolders, "Preparation of zeolite filled glassy polymer membranes," *Journal of Applied Polymer Science,* vol. 54, pp. 409-418, 1994.

[6] R. Mahajan, R. Burns, M. Schaeffer, and W. J. Koros, "Challenges in forming successful mixed matrix membranes with rigid polymeric materials," *Journal of Applied Polymer Science,* vol. 86, pp. 881-890, 2002.

[7] R. Mahajan and W. J. Koros, "Factors Controlling Successful Formation of Mixed-Matrix Gas Separation Materials," *Industrial & Engineering Chemistry Research,* vol. 39, pp. 2692-2696, 2000.

[8] Y. K. Kim, H. B. Park, and Y. M. Lee, "Preparation and characterization of carbon molecular sieve membranes derived from BTDA “ODA polyimide and their gas separation properties," *Journal of Membrane Science,* vol. 255, pp. 265-273, 2005.

[9] M. Sadeghi, M. A. Semsarzadeh, M. Barikani, and M. Pourafshari Chenar, "Gas separation properties of polyether-based polyurethane“silica nanocomposite membranes," *Journal of Membrane Science,* vol. 376, pp. 188-195.

[10] L. Ge, Z. Zhu, and V. Rudolph, "Enhanced gas permeability by fabricating functionalized multi-walled carbon nanotubes and polyethersulfone nanocomposite membrane," *Separation and Purification Technology,* vol. 78, pp. 76-82.

[11] P. S. Goh, A. F. Ismail, S. M. Sanip, B. C. Ng, and M. Aziz, "Recent advances of inorganic fillers in mixed matrix membrane for gas separation," *Separation and Purification Technology,* vol. 81, pp. 243-264.

[12] Y. Zhang, J. Sunarso, S. Liu, and R. Wang, "Current status and development of membranes for CO2/CH4 separation: A review," *International Journal of Greenhouse Gas Control,* vol. 12, pp. 84-107.

[13] D. Q. Vu, W. J. Koros, and S. J. Miller, "Effect of Condensable Impurities in CO2/CH4 Gas Feeds on Carbon Molecular Sieve Hollow-Fiber Membranes," *Industrial & Engineering Chemistry Research,* vol. 42, pp. 1064-1075, 2003.

[14] M. Sadeghi, M. A. Semsarzadeh, and H. Moadel, "Enhancement of the gas separation properties of polybenzimidazole (PBI) membrane by incorporation of silica nano particles," *Journal of Membrane Science,* vol. 331, pp. 21-30, 2009.

[15] A. K. Zulhairun, A. F. Ismail, T. Matsuura, M. S. Abdullah, and A. Mustafa, "Asymmetric mixed matrix membrane incorporating organically modified clay particle for gas separation," *Chemical Engineering Journal.*

[16] Y. W. Chen-Yang, Y. K. Lee, Y. T. Chen, and J. C. Wu, "High improvement in the properties of exfoliated PU/clay nanocomposites by the alternative swelling process," *Polymer,* vol. 48, pp. 2969-2979, 2007.

[17] X. Fu and S. Qutubuddin, "Polymer“clay nanocomposites: exfoliation of organophilic montmorillonite nanolayers in polystyrene," *Polymer,* vol. 42, pp. 807-813, 2001.

[18] T. G. Gopakumar, J. A. Lee, M. Kontopoulou, and J. S. Parent, "Influence of clay exfoliation on the physical properties of montmorillonite/polyethylene composites," *Polymer,* vol. 43, pp. 5483-5491, 2002.

[19] H.-L. Tyan, Y.-C. Liu, and K.-H. Wei, "Thermally and Mechanically Enhanced Clay/Polyimide Nanocomposite via Reactive Organoclay," *Chemistry of Materials,* vol. 11, pp. 1942-1947, 1999.

[20] J. W. Gilman, C. L. Jackson, A. B. Morgan, R. Harris, E. Manias, E. P. Giannelis, M. Wuthenow, D. Hilton, and S. H. Phillips, "Flammability Properties of Polymer Layered-Silicate Nanocomposites. Polypropylene and Polystyrene Nanocomposites " *Chemistry of Materials,* vol. 12, pp. 1866-1873, 2000.

[21] S. S. Ray, "Rheology of Polymer/Layered Silicate Nanocomposites," *Journal of Industrial and Engineering Chemistry,* vol. 12, pp. 811-842, 2006.

[22] S. A. Hashemifard, A. F. Ismail, and T. Matsuura, "Effects of montmorillonite nano-clay fillers on PEI mixed matrix membrane for CO2 removal," *Chemical Engineering Journal,* vol. 170, pp. 316-325.

[23] C. Silvestre, D. Duraccio, and S. Cimmino, "Food packaging based on polymer nanomaterials," *Progress in Polymer Science,* vol. 36, pp. 1766-1782.

[24] J. P. G. Villaluenga, M. Khayet, M. A. LÃ³pez-Manchado, J. L. Valentin, B. Seoane, and J. I. Mengual, "Gas transport properties of polypropylene/clay composite membranes," *European Polymer Journal,* vol. 43, pp. 1132-1143, 2007.

[25] H. M. C. d. Azeredo, "Nanocomposites for food packaging applications," *Food Research International,* vol. 42, pp. 1240-1253, 2009.

[26] S. A. Hashemifard, A. F. Ismail, and T. Matsuura, "Mixed matrix membrane incorporated with large pore size halloysite nanotubes (HNT) as filler for gas separation: Experimental," *Journal of Colloid and Interface Science,* vol. 359, pp. 359-370.

[27] G. Defontaine, A. Barichard, S. Letaief, C. Feng, T. Matsuura, and C. Detellier, "Nanoporous polymer " Clay hybrid membranes for gas separation," *Journal of Colloid and Interface Science,* vol. 343, pp. 622-627.