

REVIEW ARTICLE

POLYMER CLAY NANOCOMPOSITES FOR GAS SEPARATION: A REVIEW

N.M. Ismail^{1*}, A.F. Ismail², A. Mustafa², A.K. Zulhairun², F. Aziz², N. Bolong¹, A.R. Razali³¹Faculty of Engineering, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah.²Advanced Membrane Technology Research Center (AMTEC), Universiti Teknologi Malaysia 81310 Skudai Johor³Manufacturing Focus Group, Faculty of Mechanical Engineering, Universiti Malaysia Pahang, 26600 Pekan Pahang*Corresponding author Email: maizura@ums.edu.my

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ARTICLE DETAILS

Article History:

Received 01 February 2019
Accepted 01 March 2019
Available online 1 April 2019

ABSTRACT

Application of polymer clay nanocomposites for carbon dioxide (CO₂) removal in gas separation by using mixed matrix membranes is promising due to the advancement of nanotechnology and polymer processing. In this regard, as clay is abundantly available, cheaper and has attractive physical and chemical properties, the incorporation of these silicate layers within the polymer matrix as filler is favourable. In principle, the exfoliated clay single layers create higher tortuosity effects and may improve the separation properties of the membrane. This review presents a synopsis of the polymer clay nanocomposites development and applications as well as their potential for the removal of CO₂ from gas mixtures. Details of the recent works in the development of mixed matrix membranes embedded with clay for gas separation were also discussed. In addition, the problems and mechanism to evaluate the exfoliation properties were emphasized identifying the gaps and motivates for future research works utilizing clay nanoparticles as membrane filler.

KEYWORDS

Polymer clay nanocomposites, mixed matrix membrane, gas separation, intercalation, exfoliation

1. INTRODUCTION

Compared to conventional filled polymers which incorporate micron size fillers, polymer clay nanocomposites (PCNs) have received an increasing attention as a potential low-cost alternate to high-performance composites due to their improved properties of mechanical, chemical and physical structures. Applications of clay nanocomposites cover a wide range of industries, such as automotive (engine, parts, tyre), packaging, membranes, electrical insulators, coatings, flame resistance materials [1–5]. Previous studies have shown that the presence of the exfoliated clay particles provides substantial improvement on the clay-based nanocomposites which includes thermal stability and decreased flammability, higher modulus, barrier properties and increased in strength [6–10]. These will allow the nanoparticles to be used as reinforcement, barrier and electrical conductor. Many have also reported the use of organoclays as fillers for the fabrication of nanocomposite introduced into various kinds of organic-inorganic hybrid system utilizing polymers such as epoxys, polyurethanes, polyimides, polysulfone, polyethersulfone, nitrile rubber, polyesters, polypropylene, polystyrene and polysiloxanes, among others. The final properties of the nanocomposites are largely influenced by the clay's aspect ratio, dispersion and alignment as well as the polymer-polymer and polymer-clay interface interaction. There are three methods most commonly used in the fabrication of nanocomposites namely in situ intercalative polymerization, intercalation of melt and intercalation polymer from solution [11–13]. In situ polymerization requires the use of monomer to swell the silicate layers and upon subsequent polymerization, the intercalated sheets are filled with polymer chains. Melt intercalation on the other hand offers a different method in the fabrication of nanocomposite without the use of monomer or solvent. For intercalation

of polymer from solvent, dispersion of the silicate layers in a suitable solvent will swell the silicate layers and the polymer chain intercalate and displace the solvent within the gallery of the silicate. The final structure of nanocomposites is obtained by removing the solvent, usually by phase inversion in the case of asymmetric membranes or heat treatment for dense membranes. Addition of small amount of clay in the production of PCN served as an important technology for mixed matrix membranes (MMMs) fabrication. In this review, current works on polymer clay nanocomposite as MMMs and their potential for gas separation application are discussed. The importance of the silicate layers intercalated and exfoliated structure and methods to quantify them are also highlighted.

2. CLAY AS FILLER FOR MIXED MATRIX MEMBRANES

Clay minerals from smectetic group has been identified to be the potential filler with montmorillonite (MMT) being the most commonly used in nanocomposites due to its high aspect ratio and high surface area contributing to the property enhancements [14]. It is also available in large quantities, environmentally friendly and in the class of naturally occurring minerals [1]. MMT, a hydrous alumina silicate mineral, is capable of adsorbing cations such as Na⁺ or Ca⁺ due to presence of the net negative charge on the lamellar surface and comprises of lamellae constructed from octahedral alumina sheets sandwiched between two tetrahedral silicate sheets [15]. Figure 1 shows the crystal structure of the 2:1 phyllosilicates. The thickness of the layer is around 1 nm, with dimension of the layer in the range of 30 nm to microns [16]. Formation of good nanocomposites is facilitated by the existence of cationic characters on the surface which helps the intercalation with the polymer.

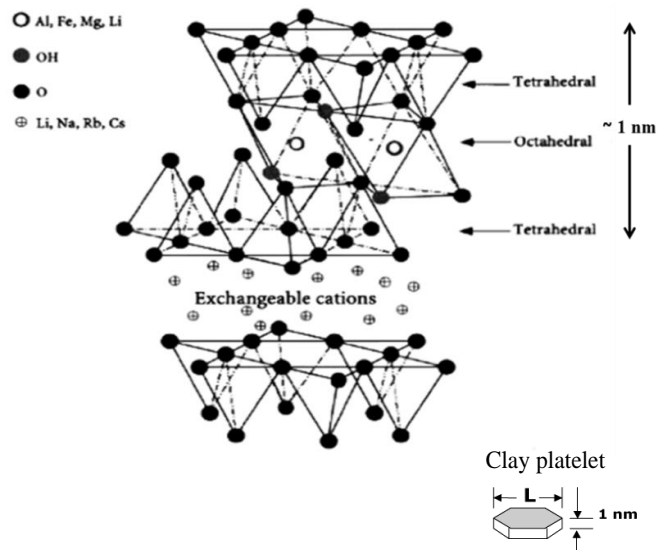


Figure 1: Ray and Okamoto

The mode of clay layers dispersion in a particular polymeric system can be manipulated resulting in different position of the layers compared to their initial state to obtain an ideal morphology. Generally, the possible layered silicate dispersion can be classified into a phase separated, intercalated and exfoliated structure as shown in Figure 2. A good dispersion (exfoliation) of clay into the polymer matrix is dependent on the compatibility between the clay and chosen polymer. Very often, surface modification through ion-exchange reactions was conducted to replace the interlayer cations with primary, secondary, or tertiary quaternary alkylammonium or alkylphosphonium cations in order to change the hydrophilicity nature of the clays for compatibility with the polymers [17].

These cations lower down the surface energy of the inorganic component and improve the wetting properties with polymer and result in a larger interlayer spacing. Additionally, it provides the functional group that reacts with the polymer and responsible for initiating polymerization of monomer, hence improving the interface between the inorganic particles and polymer [18]. The larger gas molecule has difficulty for diffusion in in the following manner; exfoliated > intercalated > phase-separated. The increase tortuosity of the silicate layers exfoliated structure as shown in Figure 3 usually reduces the permeability and consequently improves the selectivity.

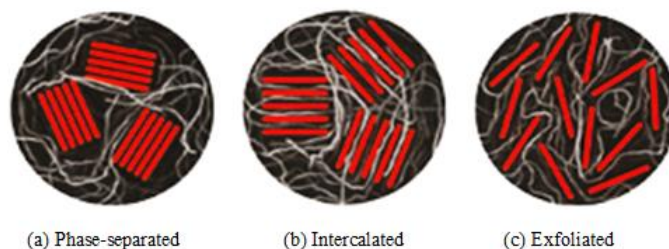


Figure 2: Types of possible clay minerals structure in polymer matrices

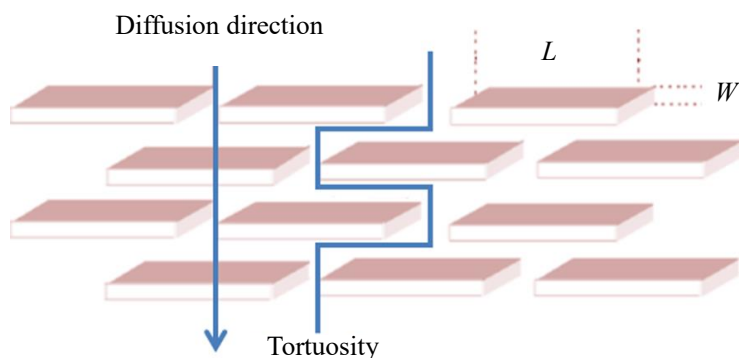


Figure 3: Ideal arrangements of orthogonally shaped platelets in a parallel array with their main direction perpendicular to the diffusion direction in barrier nanocomposites

3. RECENT PROGRESS OF CLAY BASED MIXED MATRIX MEMBRANE FOR GAS SEPARATION

Incorporation of nanoclays in the hybrid membrane provides a new approach in the development of MMMs for gas separation. Although layered silicate has been used as fillers for nanocomposites for various applications such as food packaging, ultrafiltration [19], pervaporation

[20], and in fuel cell [21], little work has been done to exploit its potential in gas separation. MMT, hectorite, and saponite are the most commonly used layered silicates and besides of the low cost and availability, few researchers have reported valuable findings for their MMMs, including Defontaine *et al.* (2010), Hashemifard *et al.* (2011), Liang *et al.* (2012), Zuhairun *et al.* (2014) [22–25] and Ismail *et al.* (2015) [19–26]. Defontaine *et al.* (2011) incorporated two types of clays in their study, sepiolite and MMT, into polydimethylsiloxane (PDMS) membrane [22]. SEM images

revealed that for lower loadings the nanoparticles are well distributed. Selectivity ratio of O₂/N₂ remained constant for both PDMS/Sepiolite and PDMS/MMT regardless of the increase in loading. CO₂/CH₄ selectivity, on the other hand, showed an increase in selectivity as the filler loading is increased. They found that in the case of Sepiolite, the separation factor increases with the clay content higher than in the pristine membrane indicating that the clay and the loadings have significant effect on the performance of the MMM. In another work by Hashemifard *et al.* (2011), they have fabricated PEI based MMM with various types of clays including raw MMT, C15A, general MMT, hydrophobic MMT and hydrophilic MMT and studied the morphological characteristics and performances for each membrane [23]. The permeation test revealed that Cloisite 15A gave the highest permselectivity among all the fillers and the results can be summarized as follows; C15A > general MMT > hydrophilic MMT >

hydrophobic MMT > raw MMT. While the selectivity experienced a dramatic increase, the permeability shows a reduction. Meanwhile, Liang *et al.* (2012) developed PES-based MMM with the incorporation of Na-MMT clays and titanium dioxide (TiO₂) nanoparticles [24]. For PES/MMT MMMs, they observed significant increase in permeabilities for CO₂ and CH₄ with the increasing filler content. However, the gas selectivity was greatly reduced. PES/TiO₂ MMMs experienced an increased selectivity at 4 wt% TiO₂ and decreased as the loading was increased. They concluded that high permeabilities and low selectivity was caused by the formation of membrane defects and polymer-filler interface voids. Recently, it has been reported that C51A was also able to improve the CO₂ permeance when incorporated in PSf and PES [25,26]. Table 1 provides the summary of the performance of some clay-filled MMMs for gas separation.

Table 1: Permeation and selectivity (α) of some clay-filled MMMs for CO₂/CH₄ separation

Polymer/Clay membrane	Performance		Ref.
	Permeability P _{CO₂}	Selectivity α	
PDMS/Sepiolite	-	14	[22]
Ultem@ 1000 PEI/Halloysite	1.45 ^a	15.12	[27]
Ultem@ 1000 PEI/Raw MMT	0.90 ^b	1.72	[23]
Ultem@ 1000 PEI/Cloisite15A	0.92 ^b	55.2	
Ultem@ 1000 PEI/ Halloysite	2.65 ^a	85.17	[28]
PES/MMT	100 ^a	0.4	[24]
Psf/Cloisite15A	74.91 ^b	20.98	[25]
PES/Cloisite15A	3.71 ^b	46.89	[26]

^a Permeation unit in Barrer ^b Permeation unit in GPU

4. QUALITATIVE AND QUANTITATIVE ANALYSIS OF CLAY DISPERSION IN POLYMER MATRIX

The clay or silicate layers exfoliation and intercalation within the polymer matrix can be quite difficult to interpret. Therefore, in order to investigate the quality of the clay dispersion within the polymer matrix, both qualitative and quantitative approaches are often necessary. It is important to have a good understanding on the dispersion degree of the silicate layers in order to correlate the microstructure with the fabrication protocol and overall membrane properties as discussed in the following sections.

4.1 Qualitative Analysis

Currently, several techniques have been applied to measure the state of clay dispersion qualitatively; WAXD, TEM, solid-state nuclear magnetic resonance (NMR), rheological techniques, mechanical testing, and atomic force microscopy [29–33]. However, WAXD and TEM are the most commonly used techniques in the literatures [30]. WAXD is preferred for material characterization because it is cheap and relatively easy and a quick technique [31]. Meanwhile, TEM provides direct in-depth observation of the microstructure of the membrane [34]. This technique was also capable of characterizing the distinct micrographs of intercalated, exfoliated and mixture of both, which is lacking in WAXD. Measurement from the TEM takes the advantage of the silicate layers characteristics while WAXD measures the degree of opening which is later translated in *d*-spacing. Increase in *d*-spacing reflects a better exfoliation of the clay structure. Hence, the use of both techniques is important to validate the morphology. Despite the aforementioned advantages, there are few challenges associated with these techniques: (1) difficulty in preparing the samples due to complex microstructure, (2) high electron

beam which can affect the membrane and (3) the low clay loading at the skin layer of the membrane. TEM observation is usually conducted for a dense membrane or nanocomposite. Ultramicrotomy procedure on asymmetric membrane, on the other hand, is quite challenging due to the presence of the sublayer which consists of larger micro and macrovoids. Slicing the membrane often ‘tears’ the sample and often revealed the surface of clay instead of the cross-section area. In addition, the area of interest for the observation is located at the skin layer. Finding the clay at the skin layer was also challenging because of the very thin skin layer. Hence, obtaining a good micrograph during TEM observation requires a series of effort and good sampling procedures.

4.2 Quantitative Analysis

Investigating the clay silicate layers dispersion by using TEM and XRD gives a general overview of the overall morphology. The resultant MMMs or nanocomposites are usually made of a very complex microstructure. Hence, to get a comprehensive spatial distribution of the clay dispersion, quantitative analysis is often necessary. Limited quantitative analysis have been reported in the literature by using several methods namely particle size measurements (PSM), particle density measurements (PDM), and free path spacing measurements (FPSM) [29,35–38]. The dispersion analysis among these methods is different and few sample characteristics and measurements have been identified as summarized in Table 2. Despite the variations, comparative study from these quantitative methods would give a good approximation of the clay dispersion. In addition, the results can also be used to validate the type of clay dispersion obtained from the qualitative analysis. Prior to measurements, the micrographs from TEM observation are transformed into high binary contrast images. Advanced imaging techniques and programming softwares are necessary to determine these parameters.

Table 2: Quantitative microscopy methods for dispersion study

Methods	Sample Type	Measurement parameters	Ref.
Particle size measurements (PSM)	Intercalated or immiscible system with the presence of larger tactoids	Clay particle length (L_{clay}), clay particle thickness (d_{clay}), correlation length (ξ_{clay}), particle aspect ratio. Higher distance shows good dispersion High aspect ratio indicates less silicate layers per tactoid and better dispersion Classified as six different groups of tactoids	[32,35,36]
Particle density measurements (PDM)	Exfoliated, intercalated or immiscible system of stacks with different size	Density of the silicate layers or tactoids over a certain area Measured by software (eg: ImageJ)	[37,38]

Free path spacing measurements (FPSM)	Exfoliated and intercalated microstructures with small size tactoids	Higher density indicates better dispersion (exfoliation) Number of squares with free particle area Low number of free particle area shows better dispersion Requires iterative procedures (eg: Matlab, ImageJ)	[29]
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5. RECOMMENDATIONS

Despite the growing interest on polymer clay nanocomposites for various applications, very few works have reported findings on the gas separation properties. As these works have shown an improvement to a great length, it is suggested that further investigation should be carried out on other polymeric materials suitable for gas separation to obtain improved separation properties with an ideal morphology. An observation on the final structure of the silicate layers arrangement within the mixed matrix membranes should also be conducted since the tortuosity is an important factor in determining the gas path. This can be achieved by performing the morphological analysis via TEM. However, observing the structure at the skin layer can be quite challenging, hence a detailed method on the sample preparation and observation should be established. Qualitative analysis can provide general estimation of the silicate layers arrangement in the polymer matrix. However, these measurements alone can be misleading due to the various resultant microstructures. Thus, further analysis should be conducted to evaluate the final morphology of the membranes. These structures can be highlighted and structurally defined quantitatively, which further verified the qualitative analysis.

6. CONCLUSIONS

From this review, it can be concluded that incorporation of clay as filler in mixed matrix membranes has the potentials in improving the CO₂/CH₄ separation performance. Disordered exfoliated structure of silicate layers can be detrimental in reducing the CH₄ permeance and improving the selectivity of MMMs. However, a thorough study on the silicate layers arrangement, particularly on an asymmetric membrane at the thin skin layer is lacking due to the difficulty of TEM observation. Therefore, a series of efforts should be focusing more on this issue in order to correlate the nanocomposites final structure and their gas separation properties based on the suggested qualitative and quantitative analysis approach.

ACKNOWLEDGMENTS

The authors wish to thank the Universiti Teknologi Malaysia through Research University Grant with vot no. QJ130000.2542.04H71, QJ130000.3009.00M02 and Universiti Malaysia Sabah for the financial support throughout this research.

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