



Asymmetric mixed matrix membrane incorporating organically modified clay particle for gas separation



A.K. Zuhairun^a, A.F. Ismail^{a,*}, T. Matsuura^{a,b}, M.S. Abdullah^a, A. Mustafa^a

^a Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor Darul Ta'zim, Malaysia

^b Industrial Membrane Research Institute, Department of Chemical and Biological Engineering, University of Ottawa, 161 Louis Pasteur St., Ottawa, ON K1N 6N5, Canada

HIGHLIGHTS

- Asymmetric mixed matrix membranes were fabricated.
- Organoclay particles known as Cloisite[®] 15A were incorporated in PSF matrix.
- Permeability of CO₂, O₂, N₂, and CH₄ increased with increasing filler loading.
- O₂/N₂ and CO₂/CH₄ selectivity was maintained up to 1 wt.% C15A loading.

ARTICLE INFO

Article history:

Received 2 July 2013

Received in revised form 9 September 2013

Accepted 14 October 2013

Available online 24 October 2013

Keywords:

Mixed matrix membrane

Layered silicate

Clay minerals

Cloisite 15A

Intercalation–exfoliation

Gas separation

ABSTRACT

Asymmetric MMMs were fabricated containing various amount of organically modified clay particle (Cloisite[®] 15A) with the main intention to investigate the gas permeation behavior of the resultant material combination. The fabricated MMMs were characterized by X-ray diffraction (XRD), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), field emission scanning electron microscopy (FESEM) and pure gas permeation testing. XRD analysis suggested that clay layers crystalline structure was slightly changed upon blending but only limited polymer chain intercalation occurred thus resulted in phase separated clay–polymer composite. The gas permeation properties were evaluated by pure gases: nitrogen, oxygen, methane, and carbon dioxide. The gas permeation rate was observed to be increasing with increasing clay content while the selectivity remained at par to that of unfilled PSF before it declined at 2 wt.% C15A loading due to filler agglomeration as confirmed by FESEM. The best results were obtained at 1 wt.% C15A loading where more than 270% enhancement in O₂ and CO₂ permeance were observed, with insignificant change in O₂/N₂ and CO₂/CH₄ selectivity compared to that of neat PSF.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The unrelenting efforts to form novel materials to surpass the 'upper bound' limitation lead to the development of state-of-the-art organic–inorganic hybrids, generically called mixed matrix membranes (MMM). MMM is comprised of discrete inorganic phase dispersed in a continuous polymer phase which brings forth novel hybrid material with synergistic advantages from each phase: high selectivity of the dispersed particle, desirable mechanical integrity, and economical processability of the polymer matrix [1]. At the early stage of MMM development, selective adsorbent or molecular sieve inorganic particles such as zeolite became the main choice for the filler material [2–4].

Nowadays, the choice for MMMs inorganic filler is not limited only to zeolite or molecular sieves anymore. Abundant novel inorganic materials have been identified to give different effects on gas

transport properties of polymeric membranes. However, the factor for the successful MMM development is heavily dependent on the selection of inorganic fillers. For example, the utilization of nonporous fillers such as silica, carbons or metal oxides has also been proven to give an attractive effect on the gas separation performance [5–7]. Clay mineral, on the other hand, is one example of nonporous particle which has not yet received large attention in MMM development for gas separation purposes even though this filler has been recognized as one of the most prominent filler in nanocomposite industries [8–10].

The most widely used clay mineral is montmorillonite (MMT). MMT is a 2:1 layer type phyllosilicate as shown in Fig. 1. The mineral is composed of two silica sheets sandwiching one alumina sheet and piling on top each other, fused by weak electrostatic interaction and van der Waals forces. The size of one silicate layer is approximately one to a few nanometers thick and hundreds to thousands nanometers in lateral dimension [11]. The galleries between these layers are commonly occupied by cations such as Li⁺, Na⁺, Rb⁺ and Cs⁺ due to the electronegativity of the layers.

* Corresponding author. Tel.: +60 7 553 5592; fax: +60 7 558 1463.

E-mail addresses: afauzi@utm.my, fauzi.ismail@gmail.com (A.F. Ismail).

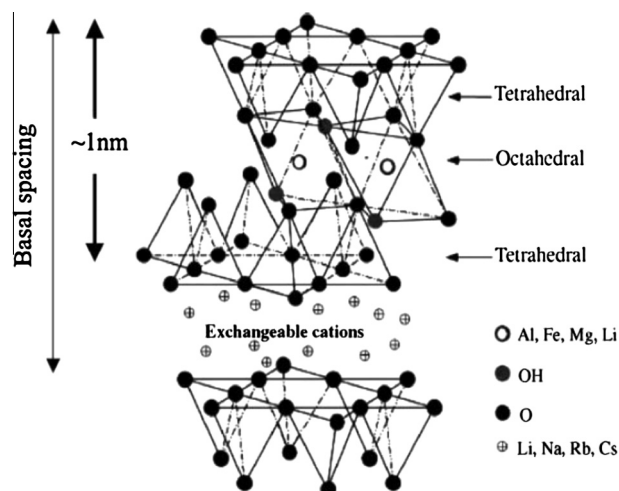


Fig. 1. Structure of 2:1 phyllosilicates.

These cations can be easily exchanged with organic surfactant or oniums to alter the surface chemistry of the clay layers for providing good compatibility with most engineering thermoplastics [8–13].

There are three types of major clay nanostructures which possibly formed in polymer matrices: the phase-separated, intercalated and exfoliated forms (Fig. 2). Generally speaking, intercalation must take place before exfoliation can be achieved. Intercalation is the insertion of molecular guests into the confined space between the interlayers of layered silicate. The intercalated structure normally interlayered by a few molecular layers of guest compound, i.e., cationic surfactants, or polymer chains. Insertion of foreign molecules into the clay lamellae results in weaker layers interaction hence the clay galleries become expanded. When the silicate layers are no longer close enough to interact with each other, the state they are in is called exfoliated state. In other words, exfoliation is achieved when the clay layers present themselves as individual thin platelets homogeneously dispersed in a matrix by an average distances. On the other hand, limited intrusion of polymer chain into the clay galleries will result in phase separated clay–polymer system [14].

In essence, the intercalation and exfoliation are the most important terms when working with clay minerals particles. The state at which the clay nanolayers are dispersed in the continuous phase will significantly alter the physico-chemical properties of the clay-hybrid materials. The influence on various material properties would greatly relies on the extent of clay layer dispersion. These nanoscale morphologies have been majorly exploited in polymer nanocomposite industries in order to provide significant improvement in mechanical strength and thermal stability of automotive parts as well as to increase the barrier properties of packaging products [15,16]. Furthermore, this mineral has also showed great

potential as filler material in improving the overall performance of polymer electrolyte membrane for direct methanol fuel cell (DMFC) application by enhancing the proton conductivity and methanol barrier properties [17,18]. It has been also used to improve the azeotropic separation of toluene/methanol mixture [19], increase the hydrophilicity of ultrafiltration membranes [20] and so on. This shows that clay mineral is one of versatile fillers which find great potential in even wider applications.

To date, experimental data on clay–polymer hybrid membrane for gas separation purpose is still diminutive in contrast to other filler–polymer combinations. Clay minerals are commonly hydrophilic in nature thus requiring certain modification to compatibilize their surface chemistry. Incorporating organically modified clays would exhibit good interaction at the filler and polymer interfaces owing to the organo-modification of the silicate layers. In fact, the compatibility of most hydrophobic thermoplastic polymers with commercially modified clay minerals has been confirmed in the literature [21–24]. Moreover, the clay modification which is commonly achieved by cationic-exchange reaction with alkylammonium surfactants will also lead to the expansion of interlayer space of the clay. The pre-expanded state of the clay layers will facilitate the intercalation of polymer macromolecules into the interlayer galleries thus rendering greater extent of interaction and dispersion of silicate layers in polymer matrix [8]. Cloisite® 15A (C15A) is an example of commercially available modified montmorillonite which will be used in this study based on previous justification. As for the continuous phase, polysulfone (PSF) is a fine choice of membrane material for gas separation due to practical combination between its permeability and selectivity in addition to its good mechanical and thermal properties as well as easy processability. It should also be noted that, most of prior studies mainly focused on characterizing dense clay–polymer hybrid films. To our knowledge, there is no documentation on the use of C15A clay mineral incorporated into polysulfone matrix for the production of asymmetric mixed matrix membrane for gas separation. In this work we will examine the impact of the C15A loading on the PSF nanocomposite physico-chemical, morphology and the gas transport properties.

2. Experimental

2.1. Materials

Polysulfone (PSF Udel-P3500) as polymer matrix phase was supplied by Amoco Chemicals. *N,N*-dimethylacetamide (DMAc), a non-volatile solvent, and tetrahydrofuran (THF), a volatile solvent were supplied by Merck and from QREc respectively. Ethanol, supplied by Merck, was used as a non-solvent additive. The inorganic filler, organically modified montmorillonite, known with the trade name Cloisite® 15A, hereafter referred to as C15A (Table 1), was purchased from Southern Clay Products, Inc., USA. PSF pellet and C15A powder were preconditioned in a vacuum oven at 80 °C for

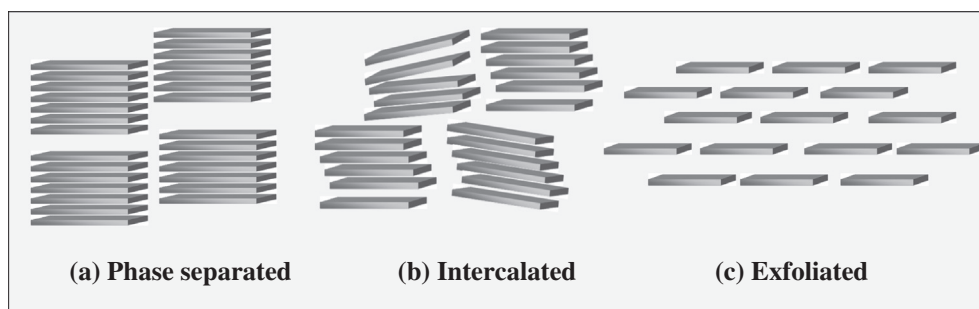


Fig. 2. Major types of clay dispersion modes: phase separated, intercalated and exfoliated form.

Download English Version:

<https://daneshyari.com/en/article/147598>

Download Persian Version:

<https://daneshyari.com/article/147598>

[Daneshyari.com](https://daneshyari.com)