



Prediction of CO₂/CH₄ permeability through Sigma-1–Matrimid[®] 5218 MMMs using the Maxwell model



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ABSTRACT

Different Sigma-1 zeolite loaded Matrimid[®] 5218 mixed matrix membranes (MMMs) were prepared by solution casting and CO₂/CH₄ gas separation experiments were performed. Also, the Maxwell model was employed to predict through the CO₂/CH₄ permeability prediction Sigma-1–Matrimid[®] 5218 MMMs. Without considering the polymer chain rigidification and the partial pore blockage effects on the Maxwell model, the AARE (average absolute relative error) values were high, i.e. for CO₂ permeability as 14.2%, for CH₄ permeability as 65.9% and for selectivity prediction as 30.5%. However, the AARE values were reduced after including the polymer chain rigidification and the partial pore blockage effects into the Maxwell model by introducing two parameters, β and α , into the model so that the AARE value for CO₂ permeability prediction was 1.6%, for CH₄ permeability prediction was 14.5% and for selectivity prediction was 15.7%.

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1. Introduction

The advantages of membrane gas separation over traditional techniques include low-energy consumption, ease of scale up, operation and control, low operating and capital investment costs and environmental friendliness [1]. A membrane is “heart” of a membrane process [2,3]. Polymeric membranes due to their advantages of low capital investment and ease of processing in modular form and high modular specific area are used in many industrial and research gas separations (natural gas processing, landfill gas recovery, olefin/paraffin separation, air separation, hydrogen recovery, etc.) [4]. However, they have limited performance in gas separation known as Robeson upper bound limit, which is a trade-off between their permeability and selectivity. Other limitations associated with conventional polymeric membranes generally are low fluxes and selectivities to process usual large volumes of gas streams and CO₂ plasticizing effect which suppresses their separation performance. These limitations constrain the spread of polymeric membrane applications in different industries [4,5].

Mixed matrix membranes (MMMs) which are formed from different organic and inorganic materials may exhibit superior separation performance due to incorporation of molecular sieves in organic polymers resulting in enhanced separation performances [3,6–13].

MMMs are typically prepared by incorporation of high separation performance inorganic molecular sieves such as zeolites or carbon molecular sieves (CMS) in polymer matrices with the aim of improving the resultant MMMs separation performances. MMMs combine the advantages of polymeric membranes with the superior separation performances of rigid molecular sieves potentially to pass gas pair Robeson upper bound limits [4,14].

The Maxwell model was originally developed for electrical conductivity in 1873 for particulate heterogeneous media composites and then used for MMMs permeability prediction in 1997 as follows [15,16]:

$$P_r = \frac{P_M}{P_c} = \frac{P_d + 2P_c - 2\phi_d(P_c - P_d)}{P_d + 2P_c + \phi_d(P_c - P_d)} \quad (1)$$

where P_r is relative permeability of MMM, P_M is MMM permeability, P_c is polymer (continuous phase) permeability, P_d filler (dispersed phase) permeability and ϕ_d is volume fraction of filler particles respectively. Several researchers used this model to predict permeability of MMMs. The Maxwell model is the most famous model for MMMs permeability prediction [3,17–19].

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The Maxwell model can be used for prediction of MMMs permeability while the filler loadings are bounded to 20% by volume. In other words, this model is used for low loading of particles in polymer matrix and this model cannot predict MMMs permeability while volume fraction of filler particles is maximum, ϕ_m , this limitation is due to an assumption of unaffected streamlines around filler particles. ϕ_m is the maximum random close packing volume fraction of filler particles. This parameter, ϕ_m , is a function of particle size distribution, particle shape, and aggregation of particles, which is 0.64 for uniform spheres. The Maxwell model also does not consider effects of particle size distribution, particle shape, and aggregation of particles [3,9].

In a MMM, if zeolite permeability is less than neat polymer permeability, with increasing zeolite loading, the MMM permeability decreases because:

$$P_r = \frac{P_d + 2P_c - 2\phi_d(P_c - P_d)}{P_d + 2P_c + \phi_d(P_c - P_d)} \times \frac{1/P_c}{1/P_c}$$

$$= \frac{(P_d/P_c) + 2(P_c/P_c) - 2\phi_d((P_c/P_c) - (P_d/P_c))}{(P_d/P_c) + 2(P_c/P_c) + \phi_d((P_c/P_c) - (P_d/P_c))}$$

$$= \frac{P_{d/c} + 2 - 2\phi_d(1 - P_{d/c})}{P_{d/c} + 2 + \phi_d(1 - P_{d/c})} \quad (2)$$

where $P_{d/c}$ is ratio of disperse permeability to polymer permeability (P_d/P_c).

P_r versus $P_{d/c}$ was plotted as shown in Fig. 1. It was observed that, P_r value decreases with reduction of $P_{d/c}$. In the other words, in a volume fraction of particles (for example $\phi_d = 0.2$), P_r (or P_M) value decreases with reduction of $P_{d/c}$ (or P_d) (as observed in Fig. 1). Furthermore, while $P_d < P_c$ (for example $P_d = 0.5P_c$ or $P_{d/c} = 0.5$), P_r (or P_M) value decreases with increasing ϕ_d .

In this research, the Maxwell model was used for prediction of CO₂/CH₄ permeability through Sigma-1–Matrimid[®] 5218 MMMs. The Maxwell model is an ideal model and does not consider undesirable effects such as polymer chain rigidification and partial pore blockage. The polymer chain rigidification and partial pore blockage effects was included in the Maxwell model and then the CO₂/CH₄ permeability through Sigma-1–Matrimid[®] 5218 MMMs was predicted using the modified Maxwell model.

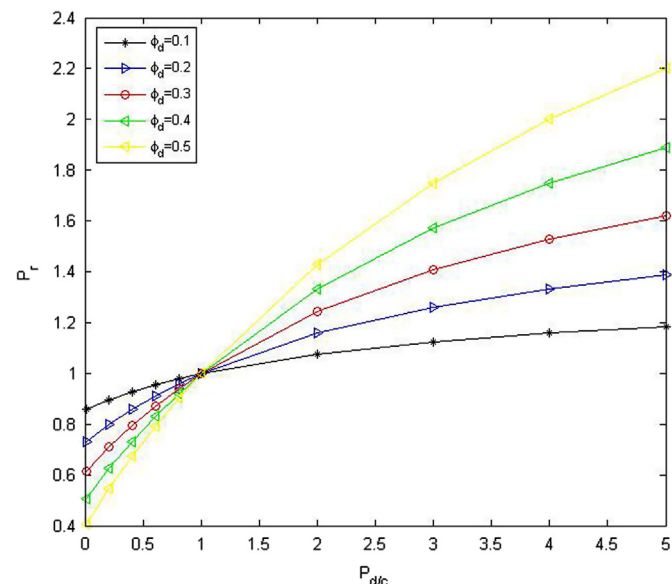


Fig. 1. Relative permeability versus $P_{d/c}$ (ratio of disperse permeability to polymer permeability) for different volume fraction of disperse particles.

2. Experimental

2.1. Materials and equipment

Sigma-1 zeolite was synthesized using 1-Adamantamine hydrochloride (1-ADA·HCl 99%, Alfa Aesar), Hydrophilic Fumed Silica (SiO₂ content $\geq 99.8\%$, Evonik Aerosil[®] 200), Sodium Hydroxide ($\geq 99\%$, Merck), and Sodium Aluminate (Na₂O 40–45% Al₂O₃ 50–56%, Merck). Matrimid[®] 5218 was purchased from Huntsman Chemical Company, USA. 1-Methyl-2-pyrrolidone (NMP, BP 204 C, $\geq 99.0\%$) was purchased from TCI America. Homemade double distilled water was used throughout the synthesis procedure. Pure gases of CO₂ (Sabalan Company, $> 99\%$) and CH₄ (Sabalan Company, $> 99.9\%$) were used for permeation measurements.

Some glass sheets, and holder meshes were used in order to prepare MMMs. A vacuum oven (Wisd, WiseVen), an oven (Memmert), some stirrers (F20 FALC, Italy), a vacuum pump (DV.3 E JB Eliminator, USA), a digital microbalance (Percisa, 310 M) and a pressure sensor (Lutron, VC-9200) were also used. Mitutoyo digital micrometer ($\pm 1 \mu\text{m}$ accuracy) was used to measure the membranes thickness. The geometrical characteristics and morphology of MMMs were observed using a VEGA\\TESCAN SEM.

2.2. Sigma-1 zeolite synthesis

Sigma-1 zeolite was synthesized hydrothermally from a synthesis solution with molar composition of 3 Na₂O:20 1-ADA: Al₂O₃:60 SiO₂:2400 H₂O [20]. The synthesis solution was prepared in two Teflon beakers. The first one was charged with double distilled water, sodium aluminate and aqueous solution of sodium hydroxide. In the other one, 1-ADA was dispersed in fumed silica and then double distilled water was added and mixed. Finally, the mixtures were combined, and the resulting mixture was stirred for 30 min. The homogenized gel was transferred to a 23 ml rotating Teflon lined autoclave heated at 453 K in an oil bath for 140 h. When the synthesis was completed, the autoclave was cooled down to room temperature and discharged. The resulting solid was collected by centrifugation, dried in air, and calcined at 773 K for 48 h to remove the organic template.

2.3. Membrane preparation

Polymers and zeolite powders were activated at 393 K under vacuum for 24 h to remove any adsorbed adsorbents. The zeolite powder (as reported in Table 1) and 10% of the total polymer were suspended in the prescribed amounts of solvent (NMP), and the mixture was stirred for 24 h at room temperature, and then the remaining polymer was added and stirred at room temperature for another 24 h. To adequately disperse the zeolite particles within the polymer matrix; the suspensions were sonicated for several 10 min periods until homogeneous suspensions were obtained. After degassing the suspensions under vacuum (-0.02 MPa , 393 K) for 4 h, they were immediately casted over clean warm (343 K) glass plates. The suspensions (2.5 ml) were casted in such manner that after the solvent evaporation, the membranes thicknesses of 40–70 μm were obtained. The formed films were peeled from the glass surfaces at high temperature (around 443 K) in order to avoid rupturing during

Table 1
Contents of the MMMs preparation solutions.

Material	Conc. (wt%)
Solvent	80
Polymer	20
Zeolite	2, 5, 10, 15, 20 (of polymer content)

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