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Evaluation of CO_2/CH_4 Gas Separation in PVA and PVC Mixed Matrix Membrane Permeation Models

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ABSTRACT

The purpose of this paper is to examine, predict and compare gas transport behavior of mixed matrix membranes (MMMs) combined with porous particles with different polymeric matrix. In this regard, composite flat sheet membranes are prepared from different amounts of poly(Polyvinyl alcohol) (PVA) and poly vinyl chloride (PVC) Gas permeability were studied for the prepared membranes. Then these membranes modelled were performed by Maxwell, and the results of Maxwell model with the experimental data were compared and the percentage of error was shown. Studied results showed that despite higher permeability emissions of carbon dioxide with PVC membrane grid with carbon nanotubes in the membrane of PVA but Maxwell model for PVA membranes without any additive as a polymeric membrane has provided more acceptable results.

Keywords: Mathematic modeling; Maxwell Model; mixed matrix membrane; PVA; CO2/CH4 separation; PVC.

1. Introduction

Typical widely throughout the chemical industries [1-4] applications are O_2/N_2 separation, H_2 recovery from process gas streams, natural gas sweetening and drying and hydrocarbon recovery from off-gas [5]. These processes have traditionally been carried out using absorption, adsorption, cryogenic and other techniques. [1, 4, 6, 7] Membranes are barriers that permit the preferential transport of certain penetrants, thereby enabling the separation of mixtures of such components. Recently, gas separation membrane technology has proved as a major gas separation technique over the traditional gas separation procedures like cryogenic distillation and pressure swing adsorption. Therefore researches on this membrane have attracted much interest and some kinds of material have been utilized for these membranes in the last two decades [8–12]. Among them, polymeric membranes have received much attention and have been used in a wide range of industrial applications [13] such as CO_2/N_2 and CO_2/CH_4 gas separation processes. These membranes offer many advantages such as low energy costs, environmental endurance, simplicity of operations and good thermal and mechanical properties. Also efforts on the novel membranes preparation with better gas separation performance (combining high permeability with high selectivity) is continuing [10]. Despite of polymeric membranes advantages, there is significant limitation in the development of newer gas separation membranes which is the important Robeson trade-off between perm-selectivity and permeability. One of the best methods to overcome this restriction is utilizing mixed matrix membranes which combine the polymers process ability with greater gas separation properties of inorganic materials. Several factors can affect the structure and consequently gas permeation properties through the polymer/inorganic MMMs including:(1) polymer and inorganic intrinsic properties, (2) morphology of MMMs, e.g. shape and size dispersion of the filler particles through polymer matrix, (3) interfacial defects such as void formation and the polymer matrix's chains rigidification around the filler particles (if any), and (4) MMMs preparation procedure. Knowing the transport properties of MMMs constituents is basic important data for their proper selection and true structure design to improve their separation performance and consequently increment of the MMMs competition for current and potential membrane gas separation In this study we modeled experimental data from published experimental works by Maxwell model and comparing ability of permeation matrix membrane . Schematic diagram of an ideal MMM showed in Fig1

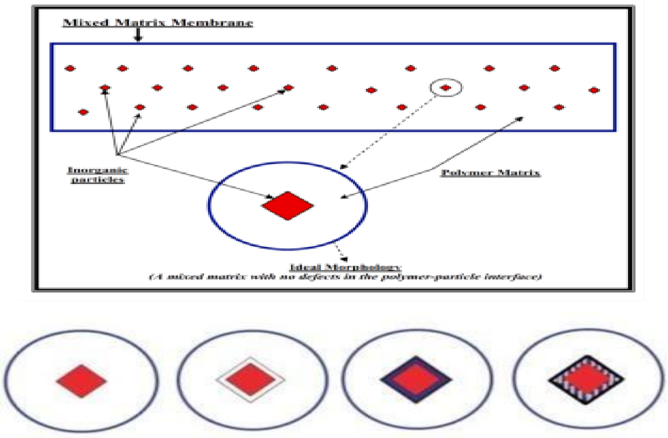

Fig 1.schematic diagram of an ideal MMM.

2. Experimental

Materials and methods

Maxwell's model is the most famous equation to predict the permeability and electrical conductivity in composite materials. Maxwell presented this equation in 1873 heterogeneous media .Development of proper model(s) for prediction of MMMs different properties, especially those of separation performance, is essential for approaching this goal. On the other hand, having of this model(s) potentially can reduce necessity of the experimental measurements' time and money for preparation and evaluation of different MMMs. Many theoretical and empirical predictive models have been adapted or developed for prediction of MMMs separation performance. The penetrates permeation through MMMs as follows:

$$P_r = P_c[\frac{P_d + 2P_c - 2\varphi_d(P_c - P_d)}{P_d + 2P_c + \varphi_d(P_c - P_d)}] \qquad (1)$$

$$\varphi = \frac{V_{fil}}{V_{fil} + V_{pol}}. \qquad (2)$$

Where Pr is the ratio of MMM permeability (PMMM) to that of continuous polymer phase (Pc) as (PMMM/Pc), Pd is the incorporated dispersed filler particles, and ϕd is the volumetric filler particles loading. Even though many other models have been proposed for predicting the permeability of mixed matrix membranes but Maxwell model has been accepted most widely in the literature .In the case of MMMs containing impermeable filler particles (Pd= 0), this model is reduced to the following equation :

$$P_r = P_c[\frac{1 - \varphi_d}{1 + 0.5\varphi_d}] \qquad (3)$$

In the present study, two mixed matrix nanocomposite membranes were comparison ability PVA/ GA /DEA , PVC/ MWCNTs for CO_2/CH_4 separation. In addition, in order to enhance the separation performance of the prepared membranes, different amounts of nano particle and different matrix to compare effect of matrix on this separation, were incorporated into the membrane matrices. It is reasonably a novel work to examine the gas separation properties of mixed matrix membranes for the CO_2 separation from natural gas (CH_4). Then we predicted performance of membrane with Maxwell model and calculated AARE%.

3. Results and discussion

As it shown Fig.2, Presented Mixed matrix membranes were successfully prepared with different PVA and PVC contents to investigate their behavior in CO_2/CH_4 separation. The results demonstrated that PVA matrix in the membranes caused a significant increase in the overall gas permeability due to chemical structure. According to the Maxwell model for impermeable filler particles, MMMs' permeability are decreased as filler particles loadings increases (Fig. 3). However, several researchers were reported some increment in permeability of MMMs with incorporated impermeable filler particles. They concluded that increasing in the resultant MMMs' permeability may be due to disrupting the polymer chain packing density by adding filler and increment of the matrix polymer's free volume, especially in the vicinity of the filler particles. It seems there is a better explanation for the case and that is the surface flux on the external surface of the incorporated filler particles. The optimization criteria of prediction accuracy of the current developed model is absolute average relative error percentage (AARE %) of predicted MMMs' permeability by the following equation :

$$AARE\% = \frac{100}{N}\sum_{i=0}^{N}\left|\frac{P_i^{cal} - P_i^{exp}}{P_i^{exp}}\right| \qquad (4)$$

Table 1 showed the Summary of the estimated filler particles' permeability and AAREs of MMMs' permeability prediction using different predictive models.

Table1: Permeability values for a) PVA and b)PVC MMMs.

AARE (%) The Maxwell model		Teorical Pr		Experimental Pr		Membrane
PCO_2	PCH_4	PCO_2	PCH_4	PCO_2	PCH_4	
55.10	55.10	0.72	0.01	1.62	0.04	PVA MMM
72.05	72.91	0.98	0.02	3.52	0.08	PVA MMM1
76.81	73.19	1.05	0.02	4.54	0.09	PVA MMM2
71.05	68.00	1.09	0.02	3.77	0.08	PVA MMM3
56.05	64.74	1.13	0.02	2.58	0.08	PVA MMM4
44.29	52.25	1.16	0.02	2.09	0.06	PVA MMM5
55.10	55.10	0.72	0.01	1.62	0.04	PVC MMM9

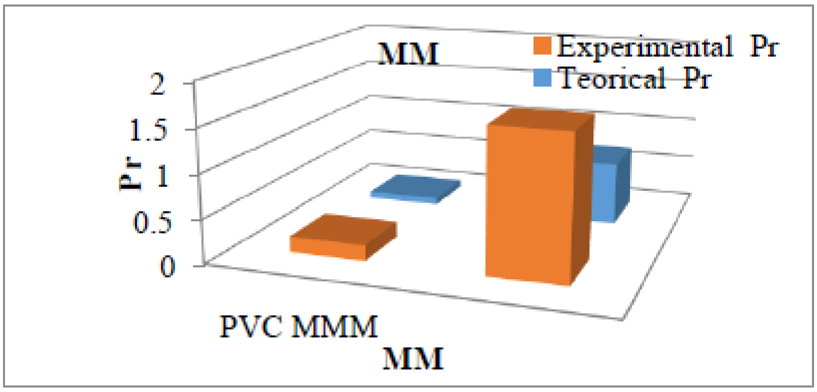

Fig.2: the polymeric matrix membranes' CO_2 permeability prediction using the Maxwell model.

4. Conclusions

Presented Mixed matrix membranes were successfully prepared with different PVA and PVC contents to investigate their behavior in CO_2/CH_4 separation. The results demonstrated that PVA matrix in the membranes caused a significant increase in the overall gas Permeability due to chemical structure. Also it is seen a significant increase in the new creation of voids.

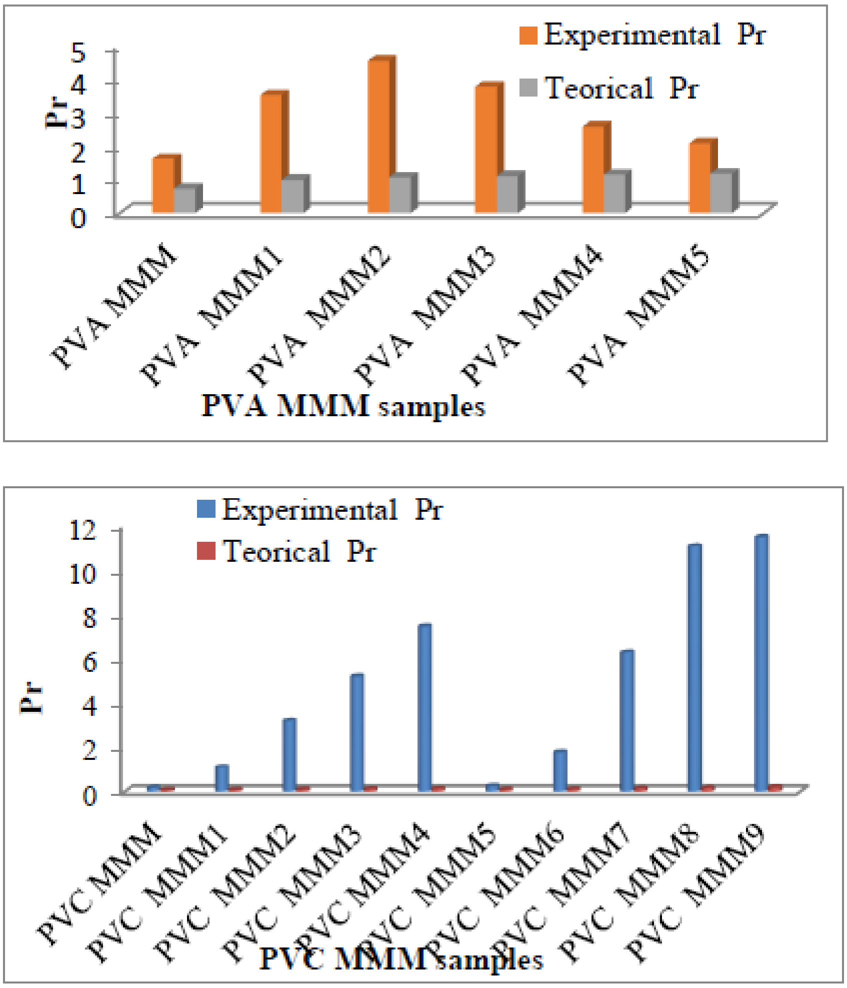

Fig.3. Effect of volumetric impermeable (e.g. Pd= 0) filler particles loadings on the MMMs' permeability prediction using the Maxwell model.

Especially adjacent to the polymer-particle interface but nano additive had a sharp improvement of adsorption ability and capacity the calculated AAREs for MMMs' permeability's were reduced considerably. The results support the aim of the current study that the incorporated nonporous filler particles are not really impermeable. Absolutely more accurate approach should be developed to provide better estimation of the so-called impermeable filler particle.

Table 2: Permeability values of membrane

AARE (%) The Maxwell model		Teorical Pr		Experimental Pr		Membrane
PCO_2	PCH_4	PCO_2	PCH_4	PCO_2	PCH_4	
55.10	55.10	0.08	٠,٠١8	0.18	0.00	PVC MMM
92.06	93.01	0.09	٠,٠١٩	1.11	0.03	PVC MMM1
96.63	97.35	0.11	٠,٠٢٤	3.22	0.09	PVC MMM2
97.60	98.15	0.13	٠,٠٢8	5.21	0.15	PVC MMM3
98.10	98.35	0.14	٠,٠٣١	7.45	0.19	PVC MMM4
55.10	55.10	0.11	٠,٠٣6	0.25	0.01	PVC MMM5
93.12	88.48	0.12	٠,٠٣٩	1.78	0.03	PVC MMM6
97.61	95.98	0.15	٠,٠٤٨	6.31	0.12	PVC MMM7
98.43	97.35	0.17	٠,٠٥6	11.08	0.21	PVC MMM8
98.29	97.14	0.20	٠,٠٦3	11.48	0.22	PVC MMM9

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