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## Comparative investigation on the correction factors of hydrogen permeability on CNTs-Mixed matrix membrane

### ABSTRACT

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This paper discusses different important gas permeation models such as “Maxwell”, “Bruggeman”, “Lewis-Neilson”, and “Pal” models to predict “Mixed Matrix Membranes” (MMMs) performance. The main parameter considered and discussed is the permeability of Hydrogen on Carbon Nanotubes (CNTs)-MMM. For evaluation of the theoretical models, experimental data of permeability for H<sub>2</sub> were compared to the theoretical models. The results revealed that, the existing models are not appropriate for evaluation of the permeability of the carbon nanostructure-based MMMs. Therefore, correction factors are needed to fit the selective permeability of carbon nanostructure-based MMMs for selective separation of various gaseous such as H<sub>2</sub> or CO<sub>2</sub>. This correction factor robustly depends on the morphology of carbon nanostructures, the defect, kind and amount of metal/metal oxide nanoparticles, doped on carbon substrate and functional groups in the carbon matrix. Hence, to be in a good agreement with experimental data for separation of H<sub>2</sub> from CO<sub>2</sub>, the correction value was estimated to -0.0022 for single-walled carbon nanotubes (SWCNTs), -0.0032 for pure multi-walled carbon nanotubes (MWCNTs), -0.0044 for carbon nanofibers (CNFs).

**Keywords:** *Mixed Matrix Membrane; Permeation model; Gas separation; Permeability.*

### INTRODUCTION

Function of membranes in gas separation process is playing an important role in lessening the operating energy requirements and environmental impact [1, 2]. Polymeric membranes have the advantages of attractive mechanical properties and economical costs. On the other hand, existing polymeric membrane materials misplace their selectivity in the presence of heavy hydrocarbons [3]. Inorganic materials can be used as membranes as a purpose of gas separation equipments [1, 4].

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Inorganic membranes like zeolite have significant advantages such as high thermal, chemical stability and good resistance at high pressures [4]. Nevertheless, the use of these materials as membranes has some limitations such as high cost production and brittleness. Thus, new types of composite membranes can be considered as permeable membrane.

(MMMs) stand for Mixed Matrix Membranes that are hybrid membranes of contain organic fillers, embedded in polymer matrix [5, 6]. MMMs have huge potentials such as good lifetime; high selectivity and permeability, superior mechanical and thermal stability that make them as a good candidate for gas separation. In recent times, "Carbon Nanotubes" (CNTs) are used as fillers in MMMs due to their important properties [6]. CNTs are known for their high surface area, active site and superior gas flux. CNTs are tubes composed of rolled-up graphite sheets with diameters in nanometer scale [7]. There are two types of CNTs [8–10]: single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs). SWCNTs are composed of a single graphene plane, while MWCNTs consist of two or more concentric tubes shells of graphene sheets. Using CNTs as dispersed fillers in MMMs offer a very attractive option approach. In order to make professional use of the MMMs, the permeability of membranes should be modeled. The existing models have been reported to predict the performance of MMMs. These models are also capable to estimate the permeability of membranes. Suitable models include "Agari", "Higuchi", "Bottcher", "Maxwell", "Bruggeman", "Pal", "Lewis-Nielsen" and "Felsk" models [11–20]. The aim of this study is to briefly discuss the existing models and also compare and evaluate the well-known theoretical gas permeation models for permeability of H<sub>2</sub> in mixed matrix membranes. This study is focused on the examination of more popular models such as the "Maxwell", "Bruggeman", "Pal", "Lewis-Nielsen" models.

## COMPUTATIONAL METHODS

Some theoretical permeation models have been used to forecast the permeation properties of MMMs as functions of the permeabilities of the continuous and dispersed phases.

The "Maxwell" model was extended for electrical conductivity of composites and can be modified by permeability as [18]:

$$P_r = \frac{P}{P_m} = \left[ \frac{2(1-\phi) + (1+2\phi)\lambda_{dm}}{(2+\phi) + (1-\phi)\lambda_{dm}} \right] \quad (1)$$

Where  $P_r$  is the permeability relation of  $P/P_m$ ,  $P$  is defined as the permeability of MMM.  $P_m$  and  $\lambda_{dm}$  are considered as the permeability of the continuous phase, and the permeability relation of  $P_d/P_m$ , respectively. Also,  $P_d$  and  $\phi$  are defined as the permeability of the dispersed phase and  $\phi$  the volume fraction of the dispersed phase, respectively. This model is appropriate to evaluate the amount of the permeability of MMM, when  $\phi$  is less than 0.2.

"Bruggeman" model was also developed to estimate the dielectric constant of composites. The equation given by:

$$(P_r)^{1/3} \left( \frac{\lambda_d - 1}{\lambda_d - P_r} \right) = (1 - \phi)^{-1} \quad (2)$$

The "Bruggeman" model has significant limitations similar to those evaluated for "Maxwell" model [13]. "Lewis-Nielsen" model originally was recommended for the elastic modulus of particulate composites [16]. To estimate the permeability

$$P_r = \frac{1+2\phi(\lambda_d-1)/(\lambda_d+2)}{1-\psi\phi(\lambda_d+2)} \quad (3)$$

Where

$$\psi = 1 + \left( \frac{1-\phi_M}{\phi_M^2} \right) \phi \quad (3a)$$

Where,  $\phi_m$  is considered as maximum packing volume fraction of nanoparticles. This is usually equaled to 0.64. This model, as clearly revealed according to Eq. (3), is easily converted to the "Maxwell" model Eq. (1), when  $\phi_m$  approaches to 1.

Also, models such as "Pal" model was originally developed for thermal conductivity. This equation is:

$$(Pr)^{1/3} \left( \frac{\lambda_d - 1}{\lambda_d - Pr} \right) = \left( 1 - \frac{\phi}{\phi_M} \right)^{-\phi_M} \quad (4)$$

In this study, the permeability as well as volume fraction of chemical vapor deposition (CVD)-fabricated MMMs using different types of carbon nanostructures such as single-walled carbon nanotubes (SWCNTs), multi-walled (MWCNTs), carbon nanofibers (CNFs) and also the effects of functional groups such as hydroxyl (OH), or carboxylic group (COOH) and the influence of metal/metal oxide nanoparticles such Fe, Pd, Cu, Ag, TiO<sub>2</sub>, doped on different forms of carbon nanostructures, were studied in detail. For this purpose, the adsorption percentages of H<sub>2</sub> were then evaluated using a lab-made thermo gravimetric analysis (TGA) instrumentation system.

for special structure like CNTs. For example, some of these models are fitting when volume fraction is low. Also, various factors related to the morphology of nanoparticles such as shape, or size distribution is ignored. This study confirms the correctness and also the precision of previously reported models for evaluation of the calculated permeability of carbon nanomaterials to H<sub>2</sub>. As shown Figure 1, differences between the experimental and theoretical models are clear. Due to the decrease of the results of theoretical models and experimental data, some correction factors should be introduced. Figure 2 shows the amount of correction factors that should be applied to the existing models. These correction factors are evaluated to -0.0022 for SWCNTs, -0.0032 for MWCNTs, -0.0044 for CNFs respectively. Applying these correction factors to the permeability coefficients of the existing models, simply makes these models suitable for prediction of the intrinsic properties CNT-based MMMs.

## RESULTS AND DISCUSSION

The previously reported models have some limitations that cause to create some errors

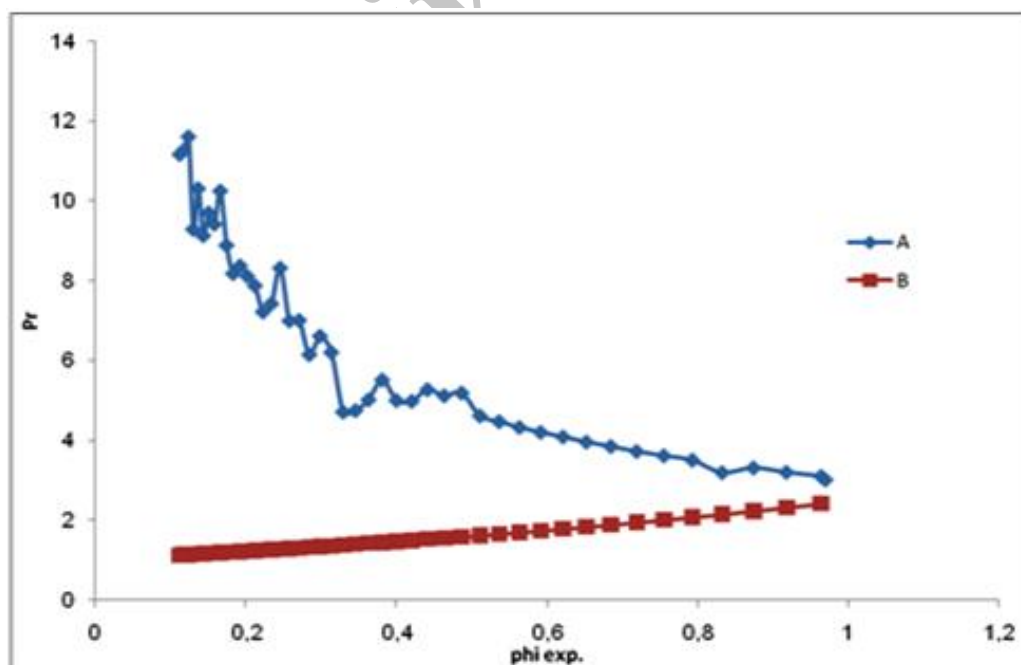


Fig. 1. Comparison between experimental and theoretical permeabilities for H<sub>2</sub>, A) Experimental B) Theoretical

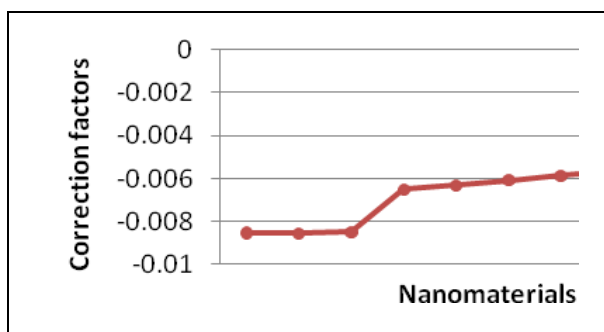


Fig. 2. Correction factors, evaluated for  $H_2$  on different forms of carbon nanostructures

## CONCLUSION

The theoretical models were developed to describe the permeability and selectivity of MMM systems. These models predicted MMM permeability but they have capability to particular fillers. The application of existing models for CNTs emerge some errors that presents the necessity to introduce the correction factors. By introducing the correction factors, the differences between experimental and theoretical models were disappeared.

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