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# Permeation models for mixed matrix membranes

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## Abstract

Permeation models for mixed matrix membranes (MMMs) are discussed. A new model is proposed for the effective permeability of a species in MMMs. The model takes into account the presence of interfacial layer (shell) at the surface of the core filler particles. According to the proposed model, the relative permeability ($P_r$) of a species in MMM, defined as permeability in MMM divided by matrix permeability, is a function of five variables, namely: ratio of interfacial shell-to-core particle radii ($\delta$), ratio of interfacial shell-to-matrix permeabilities ($\lambda_{\mathrm{Im}}$), ratio of core particle-to-interfacial shell permeabilities ($\lambda_{\mathrm{dI}}$), volume fraction of composite core–shell particles ($\phi$), and maximum packing volume fraction of particles ($\phi_m$). The predictions of the model are discussed and compared with available experimental data on permeability and selectivity of mixed matrix membranes.

*Keywords:* Mixed matrix membranes; Particulate composite; Permeability; Selectivity; Core–shell particles; Three-phase material

## 1. Introduction

Mixed matrix membranes (MMMs) are heterogeneous membranes consisting of inorganic fillers embedded in a polymer matrix [1–21]. MMMs are very effective in separation of gases (examples: separation of oxygen–nitrogen mixture, purification of natural gas by removing carbon dioxide). The inorganic fillers used in MMMs are porous molecular-sieve type materials. MMMs offer an advantageous blend of the properties of polymer matrix and filler particles. The incorporation of molecular-sieve type fillers in polymer matrix generally leads to higher permeability, higher selectivity, or both compared to the polymeric membrane. Furthermore, MMMs are easy to process and manufacture as compared with the inorganic membranes.

The molecular-sieve type fillers used in MMMs are capable of discriminating between different molecules present in the feed mixture, usually on the basis of size and shape of molecules. For example, in the separation of oxygen–nitrogen mixture Zeolite 4A is very effective as a molecular-sieve filler. Zeolites are porous alumino-silicates composed of $AlO_4$ and $SiO_4$ tetrahedra, which build up a network of cages/cavities interconnected by precisely sized apertures in the range of few Angstroms. Zeolite 4A possesses an eight-sided aperture with an effective aperture size of 3.8 Å. As this aperture size falls between the lengths of $O_2$ (length = 3.75 Å) and $N_2$ (length = 4.07 Å) molecules, Zeolite 4A acts as a molecular sieve for $O_2/N_2$ gas pair. Zeolite 4A has an $O_2/N_2$ selectivity of 37 and an $O_2$ permeability of approximately 0.77 Barrers at 35 °C [2].

Carbon molecular sieves (CMS) are also important as inorganic filler materials for MMMs. CMS are carbonaceous materials characterized by high surface area, high void volume, and a narrow pore size distribution with pores of molecular dimensions (few angstroms). CMS are industrially used for the separation and purification of gas mixtures. Gas separation in CMS materials is based on the differences in adsorption kinetics of different molecular species present in the gaseous feed mixture. For example, in the separation of oxygen–nitrogen mixture using CMS, smaller oxygen molecules adsorb more rapidly on CMS than the larger nitrogen molecules. Thus CMS materials are quite effective in separation of oxygen–nitrogen mixture; CMS have an $O_2/N_2$ selectivity of 12.5 and an $O_2$ permeability of approximately 20 Barrers at 35 °C [2].

To make efficient use of the mixed matrix membranes, the variation of permeability of a penetrant with the kind and concentration of filler materials should be known. Knowledge of

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the permeabilities of different penetrants is required for the design and operation of a MMM separation process.

In this paper, the existing models for permeation in MMMs are first reviewed, albeit briefly. A new improved model to predict the permeability of penetrants in a MMM is then proposed and evaluated using the available experimental data.

## 2. Existing permeation models

The existing models for permeation through MMMs are adaptations of thermal/electrical conductivity models. As there exists a close analogy between thermal/electrical conduction in composite materials and permeation of species through such materials, the conductivity models are readily adapted to permeability of species in MMMs.

The Maxwell model [22], originally developed for electrical conductivity of particulate composites, can be adapted to permeability as:

$$P_{\mathrm{r}} = \frac{P}{P_{\mathrm{m}}} = \left[\frac{2(1-\phi) + (1+2\phi)\lambda_{\mathrm{dm}}}{(2+\phi) + (1-\phi)\lambda_{\mathrm{dm}}}\right], \tag{1}$$

where $P_{\mathrm{r}}$ is the relative permeability of species, $P$ is the effective permeability of species in MMM, $P_{\mathrm{m}}$ is the permeability of species in the matrix (continuous phase), $\phi$ is the volume fraction of the filler particles, and $\lambda_{\mathrm{dm}}$ is the permeability ratio $P_{\mathrm{d}}/P_{\mathrm{m}}$ ($P_{\mathrm{d}}$ is the permeability of species in dispersed phase).

The Maxwell model generally describes the permeability well when $\phi$ is less than about 0.2. At higher values of $\phi$, significant deviations are expected between the predictions of Eq. (1) and actual values. Also, the Maxwell model fails to predict the correct behavior at $\phi \to \phi_{\mathrm{m}}$, where $\phi_{\mathrm{m}}$ is the maximum packing volume fraction of filler particles. Note that at $\phi = \phi_{\mathrm{m}}$, the relative permeability $P_{\mathrm{r}}$ is expected to diverge especially for MMMs with permeability ratio $\lambda_{\mathrm{dm}} \to \infty$. Furthermore, the Maxwell model does not account for particle size distribution, particle shape, and aggregation of particles.

The Bruggeman model [23], originally developed for the dielectric constant of particulate composites, can be adapted to permeability as:

$$(P_{\mathrm{r}})^{1/3}\left[\frac{\lambda_{\mathrm{dm}} - 1}{\lambda_{\mathrm{dm}} - P_{\mathrm{r}}}\right] = (1-\phi)^{-1}. \tag{2}$$

The Bruggeman model was developed using the differential effective medium approach. While the Bruggeman model is an improvement over the Maxwell model, as far as the effect of $\phi$ is concerned, it has limitations similar to that of the Maxwell model, that is, it does not give the correct behavior at $\phi \to \phi_{\mathrm{m}}$. Also, it does not account for particle size distribution, particle shape, and aggregation of particles. Furthermore, the Bruggeman model is an implicit relationship that needs to be solved numerically for the permeability.

The Lewis–Nielsen model [24,25], originally proposed for the elastic modulus of particulate composites, can be adapted to permeability as:

$$P_{\mathrm{r}} = \frac{P}{P_{\mathrm{m}}} = \left[\frac{1 + 2((\lambda_{\mathrm{dm}}-1)/(\lambda_{\mathrm{dm}}+2))\phi}{1 - ((\lambda_{\mathrm{dm}}-1)/(\lambda_{\mathrm{dm}}+2))\phi\psi}\right], \tag{3}$$

where

$$\psi = 1 + \left(\frac{1-\phi_{\mathrm{m}}}{\phi_{\mathrm{m}}^2}\right)\phi \tag{3a}$$

and $\phi_{\mathrm{m}}$ is the maximum packing volume fraction of filler particles ($\phi_{\mathrm{m}}$ is 0.64 for random close packing of uniform spheres).

The Lewis–Nielsen model, Eq. (3), gives the correct behavior at $\phi \to \phi_{\mathrm{m}}$. As expected, the relative permeability $P_{\mathrm{r}}$ at $\phi = \phi_{\mathrm{m}}$ diverges when the permeability ratio $\lambda_{\mathrm{dm}} \to \infty$. As $\phi_{\mathrm{m}}$ is sensitive to particle size distribution, particle shape, and aggregation of particles, the Lewis–Nielsen model does take into account the effects of morphology on permeability. Also note that when $\phi_{\mathrm{m}} \to 1$, the Lewis–Nielsen model reduces to the Maxwell model (Eq. (1)).

The Pal model [26], originally developed for thermal conductivity of particulate composites, can be adapted to permeability as:

$$(P_{\mathrm{r}})^{1/3}\left[\frac{\lambda_{\mathrm{dm}} - 1}{\lambda_{\mathrm{dm}} - P_{\mathrm{r}}}\right] = \left(1 - \frac{\phi}{\phi_{\mathrm{m}}}\right)^{-\phi_{\mathrm{m}}}. \tag{4}$$

The Pal model was developed using the differential effective medium approach taking into consideration the packing difficulty of filler particles. Note that when $\phi_{\mathrm{m}} \to 1$, the Pal model reduces to the Bruggeman model (Eq. (2)). The Pal model, like the Lewis–Nielsen model, gives the correct behavior at $\phi \to \phi_{\mathrm{m}}$. It also takes into account the effects of morphology on permeability through the parameter $\phi_{\mathrm{m}}$ ($\phi_{\mathrm{m}}$ is known to be sensitive to morphology). However, the Pal model, like the Bruggeman model, is an implicit relationship that needs to solved numerically for $P_{\mathrm{r}}$.

Table 1 summarizes the key aspects of the models just discussed. It appears that the Lewis–Nielsen model (Eq. (3)) is most attractive in that: (a) it is an explicit relationship simple to use; (b) it gives the correct behavior at $\phi \to \phi_{\mathrm{m}}$; and (c) it takes into account the effect of morphology through the parameter $\phi_{\mathrm{m}}$. Also note that the Lewis–Nielsen model is known to describe the conductivity of composites very well. As an example, Fig. 1 shows comparison between model predictions and experimental thermal conductivity data of particulate composites [27]. Clearly, the Lewis–Nielsen model describes the data well whereas the Maxwell model under-predicts the thermal conductivity especially at high values of $\phi$. For isometric particles (in the absence of any aggregation), $\phi_{\mathrm{m}}$ is generally taken to be 0.64 in the Lewis–Nielsen model.

## 3. Effect of interfacial layer

The models discussed in the preceding section assume ideal contact between the filler particles and matrix. More often than not, the contact between the particles and matrix phase is defective; for example, de-wetting of polymer chains from the filler surface often occurs resulting in void space between the two phases (filler and matrix). It is also possible that the polymer molecules in direct contact with the filler surface become somewhat rigidified in comparison to the bulk polymer molecules [1,3]. Thus, the permeability of a species in the interfacial region surrounding the filler particles is often significantly different from the permeability in the bulk polymer matrix.