Theoretical Models for Gas Separation Prediction of Mixed Matrix Membranes: Effects of the Shape Factor of Nanofillers and Interface Voids

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Research Article

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Theoretical Models for Gas Separation Prediction of Mixed Matrix Membranes: Effects of the Shape Factor of Nanofillers and Interface Voids

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Abstract

In this work, a new model is developed by modifying the existing Maxwell-Wagner-Sillars (MWS) model to predict the gas separation properties of mixed matrix membranes (MMMs). The new modified MWS model, for the first time, provides the simultaneous exploration of the role of nanofillers/matrix interface voids and the exact geometrical shape of nanofillers in predicting the gas separation properties of MMMs. To unveil the crucial role of nanofillers/matrix interface voids by the new model, a mixed matrix membrane is considered as a three-component system composed of the polymer matrix as the continuous component, nanofillers as the dispersed component and the interface voids between the two components. Moreover, the new model elucidates the role of the exact ellipsoidal shape of nanofillers within the membrane on the gas separation of MMMs by considering the shape factor of nanofillers. The new developed modified MWS model is accurately able to predict the gas permeation of MMMs with a lower average absolute relative error (%AARE) of around 8% compared with the around 30% for conventional models such as the Maxwell model, Bruggeman model, Lewis-Nielsen model and Pal model and even compared with the modified Maxwell model (~24%).

Keywords: Gas separation, Mixed matrix membrane, Modeling, Interface void layer, Shape factor of nanofillers
**Introduction**

The excessive amount of carbon dioxide (CO$_2$) emitted into the atmosphere should be reduced to decrease global warming, which is threatening human health and the environment [1-4]. One way of removing the carbon dioxide from the flue gas is to use membrane technology to separate and capture the CO$_2$ from nitrogen (N$_2$) [5-7]. Among different types of membrane materials, polymer membranes have been considered for CO$_2$ separation purposes due to their suitable gas separation properties, low cost and easy processing [8-12]. However, in polymer membranes, the CO$_2$/gas selectivity decreases with increasing the CO$_2$ permeability and selectivity increases with decreasing the permeability. This issue is named the trade-off challenge [13-15]. A proposed technique to solve the trade-off in polymer membranes is incorporating the inorganic nanofillers into the polymer matrix to fabricate the mixed matrix membranes (MMMs) [16-20]. MMMs combine the intrinsic properties of pure polymers, such as high permeability, and those of inorganic nanofillers, such as good selectivity.

Different types of nanofillers such as graphene oxide (GO) [21, 22], silica (SiO$_2$) [23-35] and carbon nanotubes (CNT) [36, 37] have been successfully incorporated into the membranes. In this regard, silica nanofillers have shown a considerable impact on the gas separation properties of MMMs [23-35]. Moreover, the good dispersion of nanofillers in the polymer matrix increases the thermal and mechanical properties of MMMs [38-40]. These unique properties have led to the increasing use of silica nanofillers in MMMs for gas separation applications.

Aghaei et al. [25] added silica nanofillers to the polyamide-ethylene oxide matrix to fabricate a MMM with the highest gas permeability at the silica loading of 12 wt%. They also found that the maximum CO$_2$/gas selectivity is achieved in a membrane with 10 wt% of silica nanofillers. Moreover, Ahn et al. [41] showed that embedding the silica nanofillers into the polymer matrix
increases the gas permeation through the polysulfone-MMMs. This observation is owing to the presence of voids at the interface of silica nanofillers and polysulfone matrix. In addition, it decreases the CO\(_2\)/CH\(_4\) selectivity of the MMM. Sadeghi and coworkers [42] used a MMM consisting of polyurethane and silica nanofillers to separate carbon dioxide (CO\(_2\)) from other gases such as nitrogen and methane. They found that increasing the amount of silica nanofillers to 20 wt% significantly increases the CO\(_2\)/gas selectivity of MMMs.

It is important to note that achieving a defect-free inorganic nanofillers/polymer matrix interface is the most challenging issue in fabricating MMMs. The modification of nanofillers is well known as an effective approach to enhancing the compatibility of two components [29, 31]. Moreover, the modification of the surface of inorganic nanofillers with CO\(_2\)-attractive moieties enhances the CO\(_2\) permeability and consequently the CO\(_2\)/gas selectivity of MMMs.

Owing to the significant importance of MMMs in gas separation applications, different theoretical models have been developed to predict the gas separation of MMMs [43-46]. In order to develop an efficient theoretical model for MMMs, the role of the most important parameters such as the shape of nanofillers and the gas permeability of interface voids must be considered in predicting the effective gas permeability.

**Theoretical background**

Different conventional models such as the Bruggeman model [47], Maxwell model [48], Pal model [49], Lewis-Nielsen model [50] and Maxwell-Wagner-Sillars [51, 52] were developed for the prediction of the electrical or thermal conduction of composites. However, due to the analogy of the mass transfer process with heat and electricity transfer processes, above models can also be employed for the prediction of the gas permeation of MMMs [43].
In 1873, Maxwell introduced a model for the electrical conduction process through the composites [48]. The Maxwell model was also proposed for the effective gas permeability of MMMs ($P_{\text{eff}}$):

$$
\frac{P_{\text{eff}}}{P_m} = \frac{P_f + 2P_m - 2\varphi_f (P_m - P_i)}{P_f + 2P_m + \varphi_f (P_m - P_i)}
$$

where $\varphi_f$ is the volume fraction of fillers. Also, $P_f$ and $P_m$ represent the gas permeabilities of dispersed fillers and the polymer matrix (continuous component), respectively. It is found that the Maxwell model can only be used for dilute systems with a volume fraction less than 20%.

Moreover, the Bruggeman model was proposed in 1935 for predicting the dielectric constant of composites containing fillers, which is utilized to predict the gas permeation of MMMs as [47]:

$$
\left(\frac{P_{\text{eff}}}{P_m}\right)^{-\frac{1}{3}} = 1 - \varphi_f
$$

The Bruggeman model is also able to predict the gas permeation of the membrane with a volume fraction higher than 20%. The Lewis-Nielsen model, proposed in 1973 for the elastic modulus of the fillers-containing composites, was developed to predict the gas permeation of MMMs as [50]:

$$
\frac{P_{\text{eff}}}{P_m} = \frac{1 + 2\left(\frac{P_f}{P_m} - 1\right)\varphi_f}{1 - \left(\frac{P_f}{P_m} - 1\right)\psi \varphi_f}
$$

where

$$
\psi = 1 + \left(1 - \frac{\varphi_m}{\varphi_f}\right) \varphi_f
$$

where $\varphi_m$ is the volume fraction of maximum filler packing. The value of this parameter for spherical fillers is equal to 0.64. In addition, the Pal model was proposed in 2007 to predict the thermal conductivity of the fillers-containing composites [49]. This model was developed to predict the gas permeation of MMMs as [53]:

$$
(P_{\text{eff}}/P_m)^{1/3} \left[ \frac{(P_f/P_m)^{-1}}{(P_f/P_m)^{-1} - (P_{\text{eff}}/P_m)} \right] = (1 - \frac{\varphi_f}{\varphi_m})^{-\varphi_m}
$$
The Pal model is also able to predict the gas permeation at the volume fraction of maximum filler packing.

However, despite the acceptable prediction of aforementioned models, none of them consider the effect of shape factor of dispersed fillers. To address this issue, the Maxwell-Wagner-Sillars (MWS) model has been developed for predicting the gas permeability of MMMs [51, 52]:

$$\frac{P_{eff}}{P_m} = \frac{n P_f + (1 - n) P_m + (1 - n) \varphi_f (P_f - P_m)}{n P_f + (1 - n) P_m - n \varphi_f (P_f - P_m)}$$  \hspace{1cm} (6)

In this model, $n$ is the shape factor of fillers within the membrane. The shape factor for spherical fillers is 1/3. By substituting $n = 1/3$, the MWS model reduces to the Maxwell model. In addition, substituting the shape factor of cylindrical fillers ($n = 1/6$), the MWS model reduces to the Hamilton-Crosser model [54]. However, for ellipsoidal fillers, the shape factor ($n$) is calculated as follows [55]:

$$n = \frac{1-e^2}{2e^3} \left( \ln \frac{1+e}{1-e} - 2e \right)$$  \hspace{1cm} (7)

where

$$e = \sqrt{1 - \frac{b^2}{a^2}}$$  \hspace{1cm} (8)

where $b$ and $a$ represent the minor axis and the major axis of ellipsoidal fillers, respectively. In general, theoretical models usually predict the gas permeation of mixed matrix membranes as a function of volume fraction. However, in most experimental works, the gas permeability of MMMs has been reported against the mass fraction of fillers. Therefore, to predict the gas permeability using theoretical models, the mass fraction of filler fillers within the MMM must be converted to the volume fraction of fillers. The relationship between the volume fraction and the mass fraction of fillers in the MMM is [56]:

$$\varphi_f = \frac{1}{1 + \left( \frac{1}{\varphi_{wt} - 1} \right) \left( \frac{\rho_f}{\rho_m} \right)}$$  \hspace{1cm} (9)
where $\phi_f$, $\varphi_{wt}$, $\rho_f$ and $\rho_m$ are the volume fraction of fillers, the mass fraction of fillers, the density of fillers and the density of the matrix, respectively.

The aim of this work is to develop the most accurate theoretical model to predict the gas permeation coefficient of mesoporous silica nanofiller-MMMs. For this purpose, a new model is developed to consider the effects of the exact geometrical shape of silica nanofillers within the matrix and the crucial role of polymer/nanofillers interface voids in predicting the gas separation of MMMs. In addition, the new model predictions are compared to the predictions of various conventional models including the Bruggeman model [47], Maxwell model [48], Lewis-Nielsen model [50], Pal model [49] and Maxwell-Wagner-Sillars model [51, 52].

**Methodology**

The experimental CO$_2$ and N$_2$ permeabilities of polysulfone/mesoporous silica nanofiller MMMs (PSf/MCM-48) containing different amounts of silica nanofillers (Table 1), reported in the literature [33], are used to evaluate the prediction accuracy of mentioned conventional models and the newly developed model.

### Table 1. Experimental gas permeability data of PSf/MCM-48 membranes [33]

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Permeability (Barrer)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>CO$_2$</td>
</tr>
<tr>
<td>PSf</td>
<td>4.46±0.10</td>
</tr>
<tr>
<td>PSf/MCM-48 (10 wt%)</td>
<td>8.45±0.13</td>
</tr>
<tr>
<td>PSf/MCM-48 (20 wt%)</td>
<td>18.21±0.41</td>
</tr>
</tbody>
</table>

**Results and discussion**

Figure 1a shows the experimental CO$_2$ permeability data of PSf/MCM-48 MMMs and the corresponding predictions of different conventional models against the volume fraction of
nanofillers. As can be seen, the experimental CO$_2$ permeability data are far from the predictions of conventional models. These results confirm that the conventional models cannot accurately predict the CO$_2$ permeability of PSf/MCM-48 MMMs.

In addition, comparison of the prediction results of conventional theoretical models and experimental N$_2$ permeability data of PSf/MCM-48 MMMs (Figure 1b) shows similar results of CO$_2$ permeability predictions. Therefore, as can be seen in Figure 1, the predictions of gas permeability data of PSf/MCM-48 MMMs by conventional models show significant deviations from the experimental data.

Figure 1. Comparison of conventional theoretical models and experimental a) CO$_2$, b) N$_2$ permeability data of mixed matrix membranes.

To predict the gas permeability of PSf/MCM-48 membranes, conventional models assume that the silica nanofillers are spherical. However, if the silica nanofillers are not spherical, this assumption causes an error in predicting the experimental data. The cross-sectional image of the PSf/MCM-48 mixed matrix membrane with 10 wt% of silica nanofillers using the Scanning Electron Microscopy (SEM) analysis is shown in Figure 2. As shown in Figure 2, the shape of silica nanofillers in the mixed matrix membrane is ellipsoidal. It is probably the reason for the large
deviation of predictions of the Bruggeman, Maxwell, Lewis-Nielsen and Pal models from the experimental data. Therefore, the effect of the shape factor of silica fillers on the predictions of gas permeation of MMMs must be carefully considered in the modeling. To address this issue, the MWS model (eq 6), which considers the effect of filler shape, is used to predict the experimental CO$_2$ and N$_2$ permeabilities of PSf/MCM-48 MMMs. As mentioned above, if nanofillers are assumed to be spherical ($n = 1/3$), the MWS model reduces to the Maxwell model. However, due to the non-spherical shape of silica nanofillers in PSf/MCM-48 MMMs (Figure 2), the exact value of the shape factor must be calculated and applied in the MWS model. The lengths of minor and major axes of 10 silica nanofillers observed in the SEM image (Figure 2) were averaged to obtain the exact value of the shape factor ($n$) using eq 7. The shape factor of silica nanofillers embedded in the PSf/MCM-48 mixed matrix membranes is calculated as 0.15 (Supporting Information).

![Figure 2. Cross-sectional Scanning Electron Microscopy image of the mixed matrix membrane [33]](image)

Employing the calculated shape factor ($n = 0.15$) in eq 6, the MWS model reduces to the following equation:

\[
\frac{P_{\text{eff}}}{P_{\text{m}}} = \frac{P_f + 5 \cdot 7 P_m + 5 \cdot 7 \varphi_f(P_f - P_m)}{P_f + 5 \cdot 7 P_m - \varphi_f(P_f - P_m)}
\]

(10)
The experimental CO$_2$ and N$_2$ permeabilities of PSf/MCM-48 MMMs are predicted using the MWS model for ellipsoidal nanofillers (eq 10). As shown in Figure 3, the prediction results of the MWS model are more accurate than prediction results by conventional models. These observations show that the accuracy of the MWS model is higher than those of the conventional models due to considering the real ellipsoidal shape of silica nanofillers in PSf/MCM-48 MMMs.

![Figure 3](image.png)

Figure 3. Comparison of Maxwell-Wagner-Sillars model with the experimental a) CO$_2$ and b) N$_2$ permeability data of mixed matrix membranes.

Based on these results, it is demonstrated that the exact geometrical shape of silica nanofillers plays a significant role in predicting the gas permeation coefficient of MMMs. However, the MWS model is not yet able to accurately predict the gas permeability of PSf/MCM-48 MMMs. The reason for the lack of accurate predictions of gas permeation of MMMs is that the abovementioned models neglect the effect of interface voids at the interface between silica nanofillers and the polysulfone matrix, which resulted from the incompatibility of components. However, for a real MMM, gas molecules can penetrate through three pathways including the polymer matrix, the mesoporous nanofillers and the voids at the matrix/fillers interface. Therefore, the crucial role of
voids at the interface of silica nanofillers and polysulfone matrix should be considered in modeling the gas separation through the MMMs. To develop a model that establishes the role of interface voids, in the first step, a MMM is considered as a nanofiller/interface voids/polymer matrix three-component system. Then, the three-component mixed matrix membrane is regarded to be a two-component membrane composed of a pseudo-dispersed component dispersed in the polymeric matrix. The defined pseudo-dispersed component consists of nanofillers surrounded by interface voids. In the second step, one of the mentioned conventional models such as the Maxwell model can be utilized to predict the gas permeation through the pseudo-dispersed component \( (P_{ps}) \) as [45]:

\[
P_{ps} = \frac{P_f + 2P_v - 2\varphi_z(P_v - P_f)}{P_f + 2P_v + \varphi_z(P_v - P_f)}
\]

(11)

where \( P_f \) is the gas permeation of silica fillers and \( P_v \) is the gas permeation through the interface voids (continuous component in pseudo-dispersed component). In addition, \( \varphi_z \) is the volume fraction of silica nanofillers within the pseudo-dispersed component:

\[
\varphi_z = \frac{\varphi_f}{\varphi_f + \varphi_v}
\]

(12)

where \( \varphi_v \) is the volume fraction of interface voids around the silica nanofillers in a MMM. The gas permeation through the interface voids at the silica/polysulfone interface is obtained by multiplying the solubility \( (S_v) \) and the diffusivity \( (D_v) \) of gas molecules according to the Knudsen mechanism [44]:

\[
P_v = S_vD_v = \frac{1}{RT} \left( \frac{32RT}{9\pi M} \right)^{0.5} = \left( \frac{32l_v^2}{9RT\pi M} \right)^{0.5}
\]

(13)

here \( T \) is the temperature, \( R \) and \( M \) are the gas constant and the molecular weight of the gas molecule, respectively. Moreover, the \( l_v \) parameter is the thickness of the interface voids layer.
Now, the gas permeation coefficient of MMMs ($P_{\text{eff}}$) is calculated using the modified Maxwell model as [45]:

$$\frac{P_{\text{eff}}}{P_m} = \frac{P_{ps} + 2P_m - 2(\phi_f + \phi_v)(P_m - P_{ps})}{P_{ps} + 2P_m + (\phi_f + \phi_v)(P_m - P_{ps})}$$  \hspace{1cm} (14)

To predict the gas permeation coefficient of PSf/MCM-48 membranes according to the modified Maxwell model, the thickness of interface voids, $l_v$, around silica fillers must be determined. Figure 4 shows the SEM image of a silica nanofiller in the PSf/MCM-48 mixed matrix membrane. The thickness of voids at silica fillers/polymer matrix interface is determined around 69.6 nm by averaging the values of thickness of interface void layer at five different points around the observed silica nanofiller in Figure 4, using AxioVision Rel. 4.7. software.

Figure 5 exhibits the predictions of experimental gas permeation of PSf-MCM-48 MMMs using the modified Maxwell model. The modified Maxwell model, considering the effect of interface voids, can predict the experimental gas permeation coefficient of MMMs more accurately than conventional models. However, the results of predictions using the modified Maxwell model are not in good agreement with experimental data.
As can be seen, both strategies, i.e. modification of the Maxwell model to explore the effect of interface voids (eq 14) and considering the shape factor of silica nanofillers in the MWS model (eq 10), are separately found to slightly decrease the deviation of prediction results from the experimental data. Therefore, it is expected that the combination of the two strategies in a new model results in excellent agreement between the predicted and experimental gas permeability values of PSf/MCM-48 MMMs.

For developing a new model, the MWS model, reduced by inserting the real shape factor of silica nanofillers, (eq 10) is modified by applying the role of nanofillers/polymer matrix interface voids. First, the polymer matrix/interface voids/ellipsoidal silica three-component system is regarded as a two-component system composed of the pseudo-dispersed component dispersed in the polymeric matrix. The pseudo-dispersed component consists of ellipsoidal silica nanofillers in the interface voids. The gas permeation coefficient of the defined pseudo-dispersed component ($P_{psn}$) is calculated using the MWS model (eq 10) as:

$$\frac{P_{psn}}{P_v} = \frac{P_f + 5 \cdot 7P_v + 5 \cdot 7\varphi_s(P_f - P_v)}{P_f + 5 \cdot 7P_v - \varphi_s(P_f - P_v)}$$

where $P_f$ and $P_v$ are the gas permeabilities of nanofillers and interface voids, respectively. The volume fraction of silica fillers in the pseudo-dispersed component, $\varphi_z$, and the $P_v$ are calculated using eqs 12 and 13, respectively. Finally, the effective gas permeation coefficient of MMMs is obtained using the new developed modified MWS model as:

$$\frac{P_{eff}}{P_m} = \frac{P_{psn} + 5 \cdot 7P_m + 5 \cdot 7(\varphi_f + \varphi_v)(P_{psn} - P_m)}{P_{psn} + 5 \cdot 7P_m - (\varphi_f + \varphi_v)(P_{psn} - P_m)}$$

Figure 5 also demonstrates the predictions of CO$_2$ and N$_2$ permeabilities of PSf/MCM-48 MMMs by the modified MWS model. As can be seen, the new modified MWS model has accurately predicted the experimental gas permeation of PSf/MCM-48 MMMs considering the effect of interface voids and the exact geometrical shape of silica fillers within the membrane. Therefore,
the excellent agreement of predicted gas permeation of MMMs using the new modified MWS model with experimental data indicates that the modified MWS model developed in this paper is reliable.

The validity of the new model can also be evaluated using the average absolute relative error ($\%AARE$). This parameter is used to compare the prediction results of different theoretical models and the experimental gas permeability. The $\%AARE$ value is obtained by the following equation [44, 57, 58]:

$$\%AARE = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{P_{j}^{\text{cal}} - P_{j}^{\exp}}{P_{j}^{\exp}} \right|$$

where $N$ is the number of data points. Also, $P_{j}^{\exp}$ and $P_{j}^{\text{cal}}$ are the experimental gas permeability data and the corresponding prediction results, respectively. The lower values of $\%AARE$ indicate the more accurate predictions of the experimental data using the model [44, 57, 58].

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<th>Theoretical Models</th>
<th>$%AARE$</th>
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Table 2 presents the deviations between the experimental data and the prediction results calculated using the average absolute relative error (%AARE) (eq 17). The %AARE values for predictions of CO$_2$ permeability using the different conventional models are almost the same and vary as Bruggeman model (30.63%) > Pal model (30.08%) > Maxwell model (29.96%) > Lewis-Nielsen model (29.24%). These large deviations are also observed for prediction of N$_2$ permeability using the conventional models. To decrease the deviation between predictions and experiments, the effect of the shape factor of fillers is considered using the MWS model. The %AARE values for prediction of gas permeability using the MWS model are lower than those using the conventional models (Table 2). However, the %AARE values of prediction of experimental data by the MWS model are still high. Another parameter affecting the gas permeability of MMMs is the polymer/fillers interface voids. The effect of existence of interface voids is first taken into consideration using the modified Maxwell model. The %AARE values for the prediction of experimental data using the modified Maxwell model are obtained as high as 23.30% and 23.58% for CO$_2$ and N$_2$ permeabilities, respectively (Table 2). Finally, the effects of shape factor and interface voids are simultaneously considered using the new modified MWS model. The %AARE values obtained from the predictions of experimental data using the modified MWS model are less than 8%, which
are much lower than the predictions using the abovementioned theoretical models discussed in this work.

**Conclusions**

In this work, a new model was obtained by modifying the MWS model to predict the gas separation performance of mesoporous silica nanofillers MMMs (PSf/MCM-48). To drive the new model, a MMM was accounted for as a three-component system i.e. silica nanofillers as the dispersed component, the polymer matrix as the continuous component and the interface voids between the two components. Moreover, since the silica nanofillers within the PSf/MCM-48 MMMs were ellipsoidal, the real shape factor of fillers was taken into account in the modeling.

Therefore, the newly developed model, exploring the effect of interface voids between silica nanofillers and the polymer matrix as well as the exact shape of silica nanofillers, was able to predict the gas permeation of MMMs with a lower %AARE value of around 8% compared with the around 30% for the conventional Bruggeman, Maxwell, Pal and Lewis-Nielsen models.

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**Conflict of Interest:** The authors declare that they have no competing interests.

**References**


[58] E. Chehrazi, Determination of the Thickness of Interfacial Voids in a Spherical Nanoparticles-Polymer Membrane: Fundamental Insight from the Gas Permeation Modeling, Chemical Engineering Research and Design, 177 (2022) 56-64.
Supplementary Files

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