Abstract—The purpose of this paper is to examine gas transport behavior of mixed matrix membranes (MMMs) combined with porous particles. Main existing models are categorized in two main groups; two-phase (ideal contact) and three-phase (non-ideal contact). A new coefficient, $J$, was obtained to express equations for estimating effect of the particle porosity in two-phase and three-phase models. Modified models evaluates with existing models and experimental data using Matlab software. Comparison of gas permeability of proposed modified models with existing models in different MMMs shows a better prediction of gas permeability in MMMs.

Keywords—Mixed Matrix Membrane, Permeation Models, Porous particles, Porosity.

I. INTRODUCTION

In the recent years, membrane-based gas separation is one of the challenging industries in the world. The main membrane-based separations are H$_2$/CO$_2$ separation for hydrogen production in fuel cells, CO$_2$/N$_2$ separation in flue gas or lime oven exhaust gases, CO$_2$/CH$_4$ separation for natural gas treatment or for biogas upgrading, and O$_2$/N$_2$ separation for production oxygen enriched air or pure nitrogen. Membranes are categorized based on their structure, material, modules, which indicate that material category is important. Membranes are fabricated by different materials such as polymer, ceramic, carbon, metal, and liquid [1]-[8].

Different kinds of membranes were studied for gas separation, but polymeric membranes are the most common types used for gas separation, due to proper mechanical stability, processing capability, ease of operation and importantly economical cost [1]-[6].

The main criteria of polymeric membranes are selectivity and permeability in the membrane-based separation. In Fig. 1, as can be seen, the comparison of different kinds of membrane; in addition, some limitations were observed in trade-off between permeability and selectivity of polymeric membranes at Robesson graph [1], [3], [7], [8].

To overcome the problem of trade-off between permeability and selectivity, inorganic tiny fillers dispersed in polymeric membranes were applied to improve properties of polymeric membranes. This new membrane called Mixed Matrix Membrane (MMM). Fig. 2 shows a schematic of mixed matrix membrane with different shape of particles [1]-[11].

MMMs are fabricated with different kinds of particles such as Carbon Molecular Sieve (CMS), activated carbon, silica, zeolits, nanoparticles and Metal Organic Framework (MOF) [12].

Regarding the literature [1]-[22], MMM models are categorized in two-phase and three-phase morphologies. Two-phase models are the first models in prediction of gas behavior, with assumption of ideal contact between particle &polymer and three-phase models are recommended based on weak interaction between particles and polymer matrix.

In this paper, the main existing permeation models of MMMs are reviewed. Then, the effect of porosity of particles in gas permeation through MMMs was studied. The porosity coefficient modifies existing models in two separate equations for two-phase and three-phase morphology. Gas relative permeability of modified models is validated with
experimental data and calculated gas relative permeability of existing models by least square error and Matlab software.

II. MODEL REVIEW

According to the literatures [1]-[6], [12], [16]-[21], there is a variety of permeation models for MMMs. As it was mentioned before, the main models categorized in two groups which are two-phase (particle-polymer) and three-phase (particle-interfacial layer-polymer) in Table I.

Two-phase models are based on ideal contact between polymer and dispersed phase. The two-phase models which were considered are Maxwell, Bruggeman, Lewis-Nielsen, Pal, Chiew-Galandt, Bottcher, and Higuchi. In Three-phase models is considered a non-ideal contact and poor adhesion between particle and polymer. It can cause three defects; formation of a rigidified polymer layer around inorganic fillers, pore blockage in porous particles or creation of voids between polymer and particle. Therefore, it was assumed to consider an interfacial layer between polymer matrix and dispersed phase in three-phase models [1]-[6], [14]. Models of Modified Maxwell, Felske, Modified Felske and modified Pal are in categorization of three-phase models.

III. INVESTIGATION OF PARTICLE POROSITY IN MMM MODELS

MMMs fabricated of polymeric matrix and inorganic particles for improvement polymeric membrane properties. Dispersed particles in polymeric matrix are categorized in two groups; porous and dense (non-porous) particles. In prediction of gas permeability in MMMs, Existing models has been proposed without considering particle porosity (J coefficient). J coefficient is a new factor which introduces to correct effect of particle porosity (J coefficient).

SUMMARY OF MAIN EXISTING PERMEATION MODELS FOR MMMs [1]-[24]

<table>
<thead>
<tr>
<th>Authors</th>
<th>Morphology</th>
<th>Base of model</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maxwell [1]-[6], [14]</td>
<td>Two</td>
<td>Electrical conductivity</td>
<td>$P_r = \frac{1}{\beta} \frac{1 + 2\phi(\beta - 1)/(\beta + 2)}{1 - \phi(\beta - 1)/(\beta + 2)}$</td>
</tr>
<tr>
<td>Bruggeman [1]-[6], [10],[13],[16]</td>
<td>Two</td>
<td>Thermal conductivity</td>
<td>$P_{\text{eff}} = \frac{1}{\beta} \frac{\lambda_{\text{eff}} - \lambda_f}{\lambda_f - \lambda_p}$</td>
</tr>
<tr>
<td>Lewis-Nielsen [1]-[5], [18]</td>
<td>Two</td>
<td>Permeability</td>
<td>$J = \frac{P_{\text{eff}}}{P_{\text{eq}}}$</td>
</tr>
<tr>
<td>Pal [1]-[5]</td>
<td>Two</td>
<td>Thermal conductivity</td>
<td>$P_{\text{eff}} = \frac{1}{\beta} \frac{\lambda_{\text{eff}} - \lambda_f}{\lambda_f - \lambda_p}$</td>
</tr>
<tr>
<td>Bottcher [1]-[5],[11],[8]</td>
<td>Two</td>
<td>Permeability</td>
<td>$J = \frac{P_{\text{eff}}}{P_{\text{eq}}}$</td>
</tr>
<tr>
<td>Chiew and Glandts [19],[20]</td>
<td>Two</td>
<td>Extension of Maxwell model</td>
<td>$P_{\text{eff}} = \frac{1}{\beta} \frac{\lambda_{\text{eff}} - \lambda_f}{\lambda_f - \lambda_p}$</td>
</tr>
<tr>
<td>Modified Maxwell [14],[23]</td>
<td>Three</td>
<td>Electrical conductivity</td>
<td>$P_r = \frac{2(1 - \phi) + 1 + 2\phi\beta(\phi^2)}{(2 + \phi)(1 - \phi)\beta\phi}$</td>
</tr>
<tr>
<td>Felske [14],[21]</td>
<td>Three</td>
<td>Thermal conductivity</td>
<td>$P_r = \frac{2(1 - \phi) + 1 + 2\phi\beta(\phi^2)}{(2 + \phi)(1 - \phi)\beta\phi}$</td>
</tr>
<tr>
<td>Modified Felske [1]-[3]</td>
<td>Three</td>
<td>Thermal conductivity</td>
<td>$P_r = \frac{2(1 - \phi) + 1 + 2\phi\beta(\phi^2)}{(2 + \phi)(1 - \phi)\beta\phi}$</td>
</tr>
<tr>
<td>Modified Pal [1],[3]</td>
<td>Three</td>
<td>Thermal conductivity</td>
<td>$P_r = \frac{2(1 - \phi) + 1 + 2\phi\beta(\phi^2)}{(2 + \phi)(1 - \phi)\beta\phi}$</td>
</tr>
</tbody>
</table>

$\phi$ is porosity percentage of particles

In two-phase and three-phase models in (1) and (2) respectively.

\[ J = 2 - \phi \] (1)
\[ J = 2 - \phi \] (2)

\begin{align*}
J &= 2 - \phi \\
J &= 2 - \phi
\end{align*}

In two-phase models, no defect is presumed in contact between particle and polymer. This assumption leads to gas permeability with higher error against three-phase models. This coefficient applies the effect of the interfacial layer in calculations. There is some superiority for modifications of the existing models by this method. One of the most important privileged criteria is that estimating experimental parameters such as interfacial layer permeability, thickness, chain immobilization factor, and permeability reduction factor are not essential to calculate gas permeability. However, measurements or estimating of these parameters in three-phase models are needed. But, usage of J coefficient in (1) helps to estimate precisely gas permeability in existing two-phase models. Fast and easy estimations in industrial applications are another advantage of modification by this method.
Based on three-phase morphology the effects of three defects shall be considered in three-phase modeling. These three defects are sieve in a cage, rigidified polymer layer and pore blockage. However, permeability of interfacial layer in several three-phase models included Felske and modified Felske, is estimated based on the worst cases, i.e. regidification layer and pore blockage, and It is obvious the effect of sieve in a cage and leaky case is not investigated in these models. Therefore, gas permeability in mentioned existing three-phase models is calculated lower than experimental observations. In the modified models by applying the correction of filler loading percentage in (2), the effect of sieve in a cage and leakage in interphase considered.

Modified models are reported in Table II. In this table all the existing permeation models modified with J coefficient.

<table>
<thead>
<tr>
<th>Model</th>
<th>Modified Models with J coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maxwell [1]-[6], [14]</td>
<td>( P_r = \frac{1 + 2\phi_l(\lambda_{jm} - 1) / (\lambda_{jm} + 2)}{1 + \phi_l(\lambda_{jm} - 1) / (\lambda_{jm} + 2)} )</td>
</tr>
<tr>
<td>Bruggeman [1]-[6], [10],[13],[16]</td>
<td>( P_r^{1/3} = \frac{1 - \phi_l}{\lambda_{jm} - P_r} = (1 - \phi_l)^{-1} )</td>
</tr>
<tr>
<td>Lewis-Nielsen [1]-[5], [18]</td>
<td>( P_r = \frac{1 + 2\phi_l(\lambda_{jm} - 1) / (\lambda_{jm} + 2)}{1 + \phi_l(\lambda_{jm} - 1) / (\lambda_{jm} + 2)} )</td>
</tr>
<tr>
<td>Pal [1]-[5]</td>
<td>( P_r = \frac{1 + \phi_l}{\lambda_{jm} - P_r} = (1 - \phi_l) / \phi_m )</td>
</tr>
<tr>
<td>Bottcher [1],[5],[11],[8]</td>
<td>( P_r^{1/3} = \frac{1 - \phi_l}{\lambda_{jm} - P_r} = (1 - \phi_l + \psi) / \phi_m )</td>
</tr>
<tr>
<td>Chiew &amp; Glandts [19],[20]</td>
<td>( P_r = \frac{1 + 3\phi_l + \phi_l(\psi + \phi_l) / \phi_m - \phi_l(\psi + \phi_l) / \phi_m}{(\phi_l + \psi) / \phi_m} ) ( \text{This model considered influence of three status of non-ideal contact morphology in modeling MMM. Therefore, } J \text{ coefficient factor is not essential to be used.} )</td>
</tr>
<tr>
<td>Modified Felske [1]-[3]</td>
<td>( P_r = \frac{P_m}{P_r} = \frac{1 + \phi_l}{\lambda_{jm} - P_r} = (1 - \phi_l + \psi) / \phi_m ) ( \text{This model considered influence of three status of non-ideal contact morphology in modeling MMM. Therefore, } J \text{ coefficient factor is not essential to be used.} )</td>
</tr>
<tr>
<td>Modified Maxwell [14], [23]</td>
<td>( P_r = \frac{P_m}{P_r} = \frac{1 + \phi_l}{\lambda_{jm} - P_r} = (1 - \phi_l + \psi) / \phi_m ) ( \text{This model considered influence of three status of non-ideal contact morphology in modeling MMM. Therefore, } J \text{ coefficient factor is not essential to be used.} )</td>
</tr>
<tr>
<td>Modified Pal [1], [3]</td>
<td>( P_r = \frac{P_m}{P_r} = \frac{1 + \phi_l}{\lambda_{jm} - P_r} = (1 - \phi_l + \psi) / \phi_m ) ( \text{This model considered influence of three status of non-ideal contact morphology in modeling MMM. Therefore, } J \text{ coefficient factor is not essential to be used.} )</td>
</tr>
</tbody>
</table>

IV. VALIDATION

Validity of proposed Modified models has been evaluated by least square method and compared with experimental data and existing permeation models; Maxwell, Bruggeman, Lewis-Nielsen, Pal, Chiew-Galandt, Bottcher, Felske and modified Felske. The experimental data of MMMs which are used in this paper [3] are Matrimid-5218 matrix filled with CMS for separation CO₂/CH₄ in 0.17, 0.19, 0.33, 0.36 filler loading percentage, Matrimid-5218 filled with CMS for separation O₂ of O₂/N₂ in 0.19, 0.33, 0.36 filler loading percentage, BAPD-BPADA filled with Zeolit4A for separation O₂ of O₂/N₂ in 0.15, 0.25, 0.25, 0.4 filler loading percentage, PVC filled with Zeolit4A for separation O₂ of O₂/N₂ in 0.15, 0.25, 0.4 filler loading percentage.

For an illustration for two-phase models, in Fig. 3, gas relative permeability of proposed modified model of Maxwell, Chiew-Galant, Lewis, Burggman and Pal have been compared with existing models. As can be seen in Fig. 3, modified models with considering particle porosity have better anticipation of gas relative permeability compare to existing models.

In Fig. 4, it can be seen an instance for three-phase model. The gas relative permeability of proposed three-phase model of Felske has been compared with the relative permeability of existing model. It can be observed, the modified models with considering particle porosity in their formula has a better prediction of gas relative permeability compare to existing models.

In Fig. 5, proposed modified model have been compared to two-phase and three-phase existing models by least square error values. To be more specific, among the modified models Chiew-Galanldt and modified Felske are the best models for prediction of gas behavior through this MMM.

In Figs. 6-8 also proposed modified models were checked versus existing models and experimental data, the results are similar to the gas behavior observed in Fig. 5.

Overall, not only relative permeability error of modified models are dramatically less than existing two-phase models, but also three-phase models have a better prediction compare to two-phase models. Consequently, with considering the influence of effective porosity of particles in gas permeability
calculation of MMMs, the results of modified models are precisely closer to experimental data.

Fig. 5 Comparing error percentage of exist model with improved model with J coefficient for CO₂ separation of CO₂/CH₄ in Matrimid/CMS

Fig. 6 Comparing error percentage of exist model with improved model with J coefficient for O₂ separation of O₂/N₂ in Matrimid/CMS

Fig. 7 Comparing error percentage of exist model with improved model with J coefficient for O₂ separation of O₂/N₂ in BAPD-BPADA/Zeolit4A

Fig. 8 Comparing error percentage of exist model with improved model with J coefficient for O₂ separation of O₂/N₂ in PVAC/Zeolit4A

V. CONCLUSION

In two-phase models, this coefficient considers simply effect of regidification layer and pore blockage in estimation of gas permeability in MMMs and it doesn’t need to assume interphase permeability, interfacial layer thickness and regidification factor. Therefore, with this assumption, existing two-phase models improve easily and fast.

In three-phase models, gas permeability is calculated with considering the worst condition of fabrication in MMM (regidification layer, pore blockage), therefore estimated permeability in existing three-phase models miss probability of sieve-in-cage or weak interaction between polymer and particle (void in MMMs). Thus, with correction effective pore percentage in filler loading by J coefficient, a more appropriate prediction is resulted in modified models.

In the final analysis, regarding the reasons mentioned above, it can be concluded that least square error of modified mathematical models with porosity coefficient is dramatically less than calculated error in existing models. In addition, three-phase models are in close agreement to experimental data. Therefore, it is proved that proposed modified models are nearby to experimental data and the results demonstrate a logical theory of gas behavior prediction.

NOMENCLATURE

CMS carbon molecular sieves
MMMs mixed matrix membranes
Pᵣ relative permeability
r radius of a spherical material
R distance from the center of the sieve to boundary of the polymer

Greek letters

αᵣ relative selectivity
β called matrix regidification or chain immobilization factor
δ the ratio of outer radius of regidified interfacial matrix chain layer to core radius
ψ Parameter described as function of packing volume fraction of filler particles
cfft combined sieve and rigidified interfacial matrix chain layer polymer matrix
Φᵢ the volume fraction of the filler particles
Φₛ combined volume fraction of the sieve phase and the interfacial rigidified matrix chains in the whole system.
Φ₄ volume fraction of the dispersed phase
Φ₅ maximum packing volume fraction of the dispersed phase
Φₛ volume fraction of the sieve phase in the combined sieve and rigidified interfacial matrix chain layer phase
γ parameter described for ratio of the Interphase thickness to the particle radius
ψ parameter described as function of packing volume fraction of filler particles
λ permeability ratio

Superscripts
cal calculated
exp experimental
NDP number of data points

Subscripts
d dispersed phase
i interphase
δ P refer to permeability of a penetrant in the disperse phase c
d refer to permeability of a penetrant in the continuous phase c
P permeability
M MMMs permeation prediction models: Effects of partial pore blockage
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Z. Sadeghi was born in Tehran, Iran in 1979. She got her B.Sc. in chemical
engineer from Isfahan university of Technology, Isfahan, Iran, 2003 and she
is a student in last semester M.Sc. in chemical engineering of Islamic Azad
University-Tehran North Branch, Tehran, Iran.

M.R. Omidkhah was born in Tehran, Iran in 1958. He got his B.Sc., in
chemical engineering in 1982 from Amir Kabir University of Technology,
Tehran, Iran. Also he got M.Sc.in chemical engineering in 1985 from Wayne
State University of Michigan, USA and Ph.D. in the same field in 1990 from
UMIST, Manchester, UK.

He is now President of Chemistry and chemical engineering Research
Center of Iran and a faculty member of chemical engineer department in
TarbiatModarres University. The recent journal publications are: “Hydrogen
separation and purification with poly (4-methyl-1-pentene)/MIL 53 mixed

Professor.Omidkhah is the member of IACHE (Iran Association of Chemical
Engineers).

Dr. Masoumi is the member of IAChE (Iran Association of Chemical Engineers) and IACSIT (International Association of Computer Science and Information Technology).