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Prediction of CO_2 Permeability in NH_2-MIL-53(Al)/Cellulose Acetate Mixed matrix Membranes using Theoretical Models

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Abstract: Estimation of CO_2 permeability of mixed matrix membranes (MMMs) using models has importance for the design of membrane separation system. In the current article, the previously reported models were used for the calculations of CO_2 permeability through new type of MMMs, NH_2-MIL-53(Al)/CA. It was found that modified Maxwell model demonstrated the absolute average error (AARE %) of 1.66%, which is lower than the AARE% obtained from the other theoretical models. Besides, the results also showed that AARE% of models for the prediction of CO_2 permeability was in the order of modified Maxwell model < Lewis-Nielsen model < Fleski model < Bruggeman model < Pal model< modified Fleski model < Maxwell model. Therefore, it can be concluded that modified Maxwell model is more accurate compared to other theoretical models for the prediction of CO_2 permeability through NH_2-MIL-53(Al)/CA MMMs.

Keywords: Cellulose acetate, mixed matrix membranes, CO_2 prediction, theoretical models.

1. Introduction

The presence of CO_2 in the atmosphere is the main culprit for the climate change and global warming [1-4]. On the other hand, the presence of CO_2 in natural gas caused corrosion on the pipelines in the existence of water [5-6]. Membrane separation technology is widely used for the removal of CO_2 compared to conventional typical technologies it offers advantages such as smaller foot print and less energy consumption [7]. Among the various membrane materials, mixed matrix membranes (MMMs) are widely reported for CO_2 separation because of their superior characteristics such as low cost and higher separation performance [8].

Recently, glassy polymer has gained the attention of researchers for the fabrication of MMMs for gas separation [9]. Among the various types of glassy polymer, cellulose acetate (CA) possesses few benefits of high CO_2 solubility [10]. On the other hand, metal organic frameworks (MOFs) have been extensively studied for fabrication of membranes for gas separation. Among the various MOFs, NH_2-MIL-53(Al) is a new and it exhibits attractive characteristics including high CO_2 adsorption, surface area and flexibility in pore sizes according to the applications [11-13].

In simultaneous with the growth of MMMs, numerous models have been developed to estimate the CO_2 permeation performances because of their importance for the design of membrane gas separation system [14]. Maxwell model [15-16], Bruggeman model [17], Lewis–Nielsen model [18] and Pal model [19] are considered as basic models for the prediction of CO_2 permeability in MMMs.

Maxwell model is the foundation for all theoretical models. It is simple and required less assumptions for the prediction of gases permeability [20-21]. Mahajan and Koros [22-23] predicted CO_2 permeability of zeolite A/PVAc and zeolite A/Ultem MMMs using Maxwell model. Absolute average relative error (AARE%) of 0.10% and 0.49%, were obtained respectively, However, Maxwell model does not considered the particle distribution [15]. Therefore, it showed significant AARE% of 26.04% during the prediction of CO2 permeability via CMS/Mitrimid MMM [24]. Subsequently, Bruggman model [17] is considered as modified form of Maxwell model. However, it showed significant AARE% of 21.1% for IRMOF-1/Matrimid MMM in CO_2 permeation [25]. Besides, it's also facing certain limitations for example; particles distributions are not taken into the account in the model [15].

In another work, Lewis–Nielsen [18] model has been validated by Hoang et al. [26] over CMS/Matrimid MMM in CO_2/CH_4 separation. Even though few studies have validated this model for the prediction of CO2 permeability of MMMs, this model did not account for the morphology of the fillers in MMMs [26]. Therefore, Pal model has been proposed as an extension of Lewis–Nielsen model. Rafiq et al. [27] applied Pal model to predict CO_2 permeability across the nano-silica/PSF MMMs. The AARE% obtained was 35.61% in comparison with the experimental data. Subsequently, Sanaeepur et al. [20] presented an extensive discussion on the reliability of Felske model [18]. The AARE% obtained for CO_2 permeability through the Felske model was 31.07%. Unfortunately, Felske did not account for polymer chain rigidification factor and it is also facing

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with an issue of long computational procedure. Therefore, further modification of model was done by Pal and his co-workers [19]. Consequently, Shimekit et al. [24] reported the AARE% of 4.5% over the CMS/Matrimid MMM in CO_2 separation using modified Felske model even though the computational procedure of this model is complex [20].

On the other hand, modified Maxwell model is widely used compared to the other theoretical models because of its simple formulation and easy computation [28-29]. Furthermore, modified Maxwell accounts for the interfacial defects (θi) and polymer chain rigidification (β) factors which are not considered by the other models. Recently, Xiao et al. [11] has validated the CO_2 permeability using modified Maxwell model over NH_2-MIL-53(Al)/6FDA-ODA MMM. They found that the predicted CO_2 permeability showed the deviation of 4.5% from the experimental value.

On the basis of above discussion, prediction of CO_2 permeability over NH_2-MIL-53(Al)/CA MMM is scarcely found in the literature. In the current article, the previously reported models were used for the calculations of CO_2 permeability through new type of MMMs, NH_2-MIL-53(Al)/CA. The results are compared with the experimental data reported in our previous work [30]. Lastly, AARE % of each theoretical model is calculated between the predicted and experimental CO_2 permeability.

2. Materials and Methods

The experimental CO_2 permeability results were obtained using NH_2-MIL-53(Al)/CA MMMs fabricated in the previous work [30]. Subsequently, modeling parameters including, correction factor (Ψ) of MMMs were calculated using Sargsyan method [25] and also differential scanning calorimetric (DSC) results obtained in our previous work [30]. Besides, CO_2 permeability (Pd) and maximum volume fraction (θm) of NH_2-MIL-53(Al) were obtained from the reported literature [11,31]. Theoretical models used in the current study over the MMMs including Maxwell [15], Modified Maxwell [16], Bruggeman [17], Lewis–Nielsen [18], Pal model [19] and Fleski [20] are shown in equations (1-7), respectively as follows;

$$P = P_c\left[\frac{P_d + 2P_c - 2(\theta_d)(P_c - P_d)}{P_d + 2P_c + (\theta_d)(P_c - P_d)}\right] \quad (1)$$

$$P_{bs} = P_i\left[\frac{P_d + 2P_i - 2(\theta_s)(P_i - P_d)}{P_d + 2P_i + 2(\theta_s)(P_i - P_d)}\right] \quad (2)$$

$$\frac{P}{P_c} = \frac{1}{(1-\theta_d)^3}\left[\frac{\frac{P}{P_c} - \frac{P_d}{P_c}}{1 - \frac{P_d}{P_c}}\right]^3 \quad (3)$$

$$\frac{P}{P_c} = \frac{1 + 2\theta_d(P^* - 1)/(P^* + 2)}{1 - \theta_d\psi(P^* - 1)/(P^* + 2)} \quad (4)$$

$$\left(\frac{P}{P_c}\right)^{1/3}\left[\frac{\frac{P_d}{P_c} - 1}{\left(\frac{P_d}{P_c}\right) - \left(\frac{P}{P_c}\right)}\right] = \left[1 - \frac{\theta_d}{\theta_m}\right]^{-\theta_m} \quad (5)$$

$$\left(\frac{P}{P_c}\right)^{1/3}\left[\frac{\frac{P_d}{P_c} - 1}{\left(\frac{P_d}{P_c}\right) - \left(\frac{P}{P_c}\right)}\right] = \left[1 - \frac{\theta_d}{\theta_m}\right]^{-\theta_m} \quad (6)$$

$$\frac{P}{P_c} = \frac{1 + 2\theta_d(\beta - \gamma)/(\beta + 2\gamma)}{1 - \psi\theta_d(\beta - \gamma)/(\beta + 2\gamma)} \quad (7)$$

Consequently, modeling parameters were substituted into equations (1) to (10) in order to predict the CO_2 permeability through the models. In the next step, the predicted results were compared with the experimental CO_2 permeability of NH_2-MIL-53(Al)/CA MMMs and AARE% of each model was calculated using equation (11) as follows [21]:

3. Results and Discussion

3.1 Identification of modeling parameters

Modeling parameters of NH_2-MIL-53(Al)/CA MMMs are presented in Table 2. As shown in Table 2, when the loading of NH_2-MIL-53(Al) in MMMs increases from 0 wt% to 20 wt%, the NH_2-MIL-53(Al) volume fraction (θ_d), interfacial defects (θ_i) and correction factor (Ψ) are increased from 0.14 to 0.43, 0.16 to 0.48 and 1.09 to 1.31, respectively. The increment in the volume fraction (θ_d) could be due to the increment in filler loading which increases the viscosity of the NH_2-MIL-53(Al)/CA solution and thus, stress is developed between CA and NH_2-MIL-53(Al) filler [32]. This stress may develop the pseudo dispersed phase in the CA polymer which can increase the interfacial defects (θ_i) in MMMs [12, 33-34]. Furthermore, it has been found that the correction factor (Ψ) is directly proportional to the volume fraction (θ_d) of NH_2-MIL-53(Al) and thus, it was also increased from 1.09 to 1.31 with the increment of NH_2-MIL-53(Al) loading from 5 wt% to 20 wt%.

Table 2: Modeling parameters of NH_2-MIL-53(Al)/CA MMMs.

Filler (wt%)	θ_d	$*P_c$	$*P_{bs}$	T_g	θ_i	θ_s	Ψ
0	-	15.6	-	197.3	-	-	-
5	0.14	24.7	90.2	201.5	0.16	0.62	1.09
10	0.25	39.3	90.5	205.3	0.33	0.62	1.17
15	0.35	52.6	90.6	209.6	0.45	0.63	1.25
20	0.43	43.8	90.4	214.5	0.48	0.62	1.31

Referring to Table 2 also, it is observed that CO_2 permeability of pseudo dispersed phase (P_{bs}) of MMMs increases from 90.25 Barrer to 90.68 Barrer with the increment of NH_2-MIL-53(Al) loading from 5 wt% to 15 wt%. However, further increment of NH_2-MIL-53(Al) loading from 15 wt% to 20 wt% resulted in the drop of P_{bs} of MMM. The reduction of P_{bs} could be attributed to the agglomeration of the NH_2-MIL-53(Al) particles in the MMM as verified in our previous work [30]. Furthermore, reduction in volume fraction of (θ_s) pseudo dispersed phase from 0.63 to 0.62 also supports the drop of P_{bs} of MMM.

On the other hands, CO_2 permeability (P_d) and maximum volume fraction (θ_m) of NH_2-MIL-53(Al) of 2.84 x 10^{15} Barrer, and 0.64 were obtained from the literature, respectively [11,31]. However, chain rigidification factor (*β*) of CA was remained constant at 1 as reported in the literature [20].

3.2 Prediction of CO_2 permeability

Figure 1 shows the experimental and predicted CO_2 permeability of NH_2-MIL-53(Al)/CA MMMs. From Figure 1, it has been found that CO2 permeability predicted through Maxwell model, Bruggeman model, Lewis−Nielsen model, Felske model and Pal model showed the deviation from those results obtained experimentally over the NH_2-MIL-53(Al)/CA MMMs. This result could be due to non-ideal morphology of MMMs obtained. However, the non-ideal morphology is not taken into the account during the prediction of CO_2 permeability through these theoretical models [1]. Therefore, these models could not predict the CO_2 permeability of NH_2-MIL-53(Al)/CA MMMs accurately and thus, deviation from the experimental results is observed. Lewis-Nielsen model, Fleski model, Bruggeman model, Pal model and Maxwell model demonstrated significant AARE% of 15.75%, 17.33, 22.73%, 26.69 and 30.69%, respectively.

On the other hand, predicted CO_2 permeabilities of MMMs through modified Fleski model also showed deviation from those experimental results. This result could be because of chain rigidification of polymer matrix in MMMs which reduces the diffusion of CO_2 in MMMs. However, modified Fleski model did not account the chain rigidification factor and thus, high AARE% of 28.35% was obtained [20].

As shown in Figure 1, predicted CO_2 permeabilities of MMMs through modified Maxwell model were comparable with those experimental results. The least deviation of predicted CO_2 permeabilities from the experimental result is because of the non-ideal effects such as interfacial defects, particle size, distribution and chain rigidification, which were taken into the account in modified Maxwell model [28]. Hence, relatively low AARE% of 1.66% was obtained compared with the other theoretical models. Overall, AARE% of the models used for the prediction of CO_2 permeability of NH_2-MIL-53(Al)/CA MMMs is achieved in the order as follows; modified Maxwell model < Lewis-Nielsen model < Fleski model < Bruggeman model < Pal model< modified Fleski model < Maxwell model.

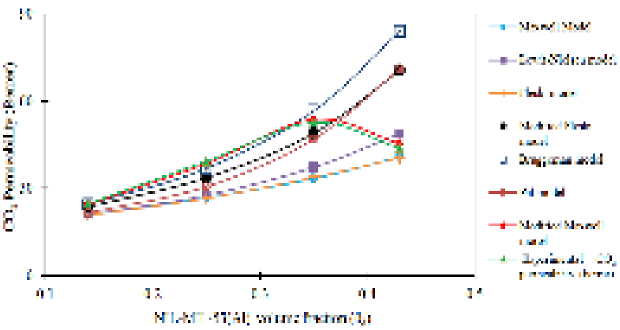

Figure 1: Experimental and predicted CO_2 permeability of NH_2-MIL-53(Al)/CA MMMs.

4. Conclusions

In summary, models have been applied to calculate the CO_2 permeability of NH_2-MIL-53(Al)/CA MMMs. Modified Maxwell model showed the AARE% of 1.66% over NH_2-MIL-53(Al)/CA MMMs, which is lower than the other theoretical models. This result is attributed to the particles size, interfacial defects and chain rigidification factor which have been considered by the modified Maxwell model. Subsequently, accuracy of models for the prediction of CO_2 permeability of MMMs were in the order of modified Maxwell model < Lewis-Nielsen model < Fleski model < Bruggeman model < Pal model< modified Fleski model < Maxwell model. Hence, modified Maxwell model is an appropriate model which can accurately predict the CO_2 permeability of NH_2-MIL-53(Al)/CA MMMs.

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