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A comprehensive computational strategy for fitting experimental permeation data of mixed matrix membranes

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ABSTRACT

A novel computational model-based strategy was developed for fitting experimental gas permeation data of mixed matrix membranes. Pore filler blockage, polymer chain rigidification and interface voids can simultaneously be taken into account in order to estimate morphological property as well as gas separation performance of MMMs. The proposed strategy was validated using several available literature data and an excellent agreement between the model predictions and experimental data was observed.

1. Introduction

Membrane-based processes are likely to play a great important role in developing energy-efficient, environmentally friendly and economic separation technologies with global issues such as CO_2 capture, natural gas and water purifications owing to their high stability, reliability, high-energy efficiency, and ease of operation [1]. Mixed-matrix membranes (MMMs) are heterogeneous membranes that contain inorganic fillers dispersed in an organic polymer matrix. MMMs exhibit the superior permeation performances of the former and good processablility, low capital cost and mechanical properties of the later [2]. The inorganic MMM fillers are mostly porous particles, including zeolites and carbon molecular sieves [3–5]. Metal-organic frameworks (MOFs) are alternative promising materials as MMM's fillers due to their large surface area, tunable pore size and diversified topology, however, their applications are still in their infancy [6].

A key challenge in developing new MMMs is the needs to describe their nano-scale morphology as well as to theoretically model their transport properties, which can provide quantitative predictions of the membrane performance of new MMMs. The transport behaviors of MMMs are strongly related to their membrane morphology. In general, there are four possible basic MMM morphologies (Fig. 1) [2,4,5]. Case I represents an ideal but difficult-to-obtain morphology, which consists of inorganic fillers and polymer matrix with no defects and no distortion at the filler-polymer interface. For estimating MMM membrane properties of particulate composite materials, various theoretical ideal models (Case I) such as the Maxwell, Bruggeman, Böttcher and Higuchi, Lewis–Nielsen, Pal, Looyenga, Gonzo–Parentis–Gottifredi, Funk–Lloyd, Kang–Jones–Nair have been proposed [5]. These models were adapted for prediction of permeation through MMMs as functions of three experimental parameters, including penetrant's permeabilities of the two phases (P_d and P_c), as well as an adjustable parameter, namely the dispersed filler loading (for example, volume fraction ϕ_d) [2,4,5]. Good agreements between experimental data and predicted values obtained from these ideal models were, however, reached with only the MMMs having low filler loading (below 20 vol%).

The different ideal morphology models amount to combining in different ways two simple hypothetical limit trajectories of the penetrant in the two-phase filler-polymer membrane. These trajectories include both a series and parallel two-layer models. The series two-layer model yields a minimum permeability (P_{Ms}) value:

$$\frac{1}{P_{Ms}} = \frac{\phi_d}{P_d} + \frac{(1-\phi_d)}{P_c} \quad (1)$$

whereas the parallel two-layer model provides a maximum permeability (P_{Mp}) value:

$$P_{Mp} = \phi_d P_d + (1-\phi_d) P_c \quad (2)$$

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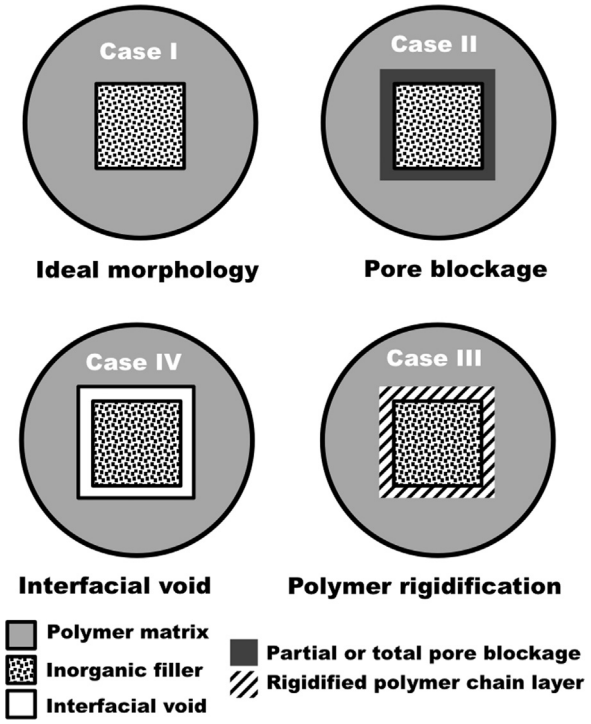

Fig. 1. Representative morphologies of mixed matrix membranes.

Another series of more realistic models has been developed in order to introduce some representation of non-ideal defective filler-polymer interface. Actually, these kinds of defects have been considered including total or partial pore blockage (Case II), polymer chain rigidification (Case III) and interfacial voids (Case IV). Mahajan et al. first proposed the concept of a pseudo-dispersed phase comprising the filler particle surrounded by an interfacial phase of thickness (l_I) [7]. As shown in Fig. 1, this interfacial phase may alternatively represent interfacial voids, partial or total pore blockage and rigidified polymer chain layers. These more sophisticated models include the modified Maxwell, modified Lewis–Nielsen, original and modified Felske, modified Pal and Hashemifard–Ismail–Matsuura models [2,4,5].

In addition to P_d, P_c, and ϕ_d, these models involve at most three other adjustable parameters, namely the interface thickness (l_I), the pore blockage factor (α), defined as

$$\alpha = \frac{P_d - P_d^*}{P_d} \tag{3}$$

and the polymer chain rigidication factor (β) given by

$$\beta = \frac{P_c}{P_c^*} \tag{4}$$

where, P_d^* and P_c^* are the corrected expressions of P_d and P_c to be introduced in Eqs. (1) and (2) in order to take these defective interphases into consideration in calculation of P_{Ms} and P_{Mp}.

In addition to these adjustable parameters, the average size (r_d) of the dispersed phase is usually established experimentally and may therefore be considered a non-adjustable parameter. The whole particle size distribution is never taken into consideration.

The sensitivity of the calculated permeation value to the parameter (l_I) was not always recognized even though both micro-photographic evidence as well as experimental results indicates this parameter (or any other adjustable parameters derived from it) may vary over large ranges.

In deriving different representations for non-ideal MMM permeation, different authors used various forms of adjustable parameters essentially related to the six ones designated above. For example in case of pore blockage (Case II), Li et al. used two parameters (β' and r'), where the β' factor is related to the average reduced gas permeability in the partial pore blockage region, and r' is the average thickness of this layer [8]. Gheimasi et al. proposed only a parameter (α as defined in Eq. (3)), indicating the extent of pore blockage, which ranges from zero (ideal morphology) to one (totally blocked pores), to describe the reduction in pure filler membrane permeability under pore blockage by polymer chains [9]. For polymer chain rigidification (Case III), permeability of the interphase layer is assumed to be defined similarly to P_c^* in Eq. (4) (β; $\beta=1$: ideal morphology; $\beta>1$: non-ideal morphology). Volume fraction of the interphase layer in the whole MMM membrane is related to the interphase thickness (l_I). This parameter has first been introduced in the modified Maxwell model as follows [8]:

$$\phi_s = \frac{\phi_d}{\phi_d + \phi_I} = \frac{r_d^3}{(r_d + l_I)^3} \tag{5}$$

In the modified Lewis–Nielsen, original and modified Felske, modified Pal and Hashemifard–Ismail–Matsuura models, this factor is converted into the δ (also designated as θ) parameter, which is the ratio of the outer radius of the rigidified polymer layer (r) to core radius of the dispersed filler particles (r_d) [10]. For the void defect (Case IV), the two required parameters are the effective thickness of the void region (l_V) and the penetrant's permeability in this region (P_V). P_V is often calculated as the product of the Knudsen diffusion coefficient (D_{Kn}) through an effective pore with the same size as the effective thickness (l_V) and the sorption coefficient of gas in the void assuming atmospheric pressure ($S=1/RT$, where R is the gas constant and T is the Kelvin temperature) [11].

Clearly, for any case of real MMMs, solving a model of permeation with multiple adjustable parameters is a complex mathematical problem. In order to simplify this problem, authors have lowered the number of adjustable parameters either arbitrarily or by using independent experimental determinations of some of the parameters such as r, r', l_I, l_V, and filler permeability, P_d, and even α, β or β' [5,8,10].

In a case of void defect (Case IV), Chaidou et al. also solved the modified Maxwell model with two adjustable parameters (P_d and l_V) by minimizing the square of the differences between the experimental permeability data and the predicted values. P_c and ϕ_d are known parameters, whereas α and β are respectively hypothesized to be zero (no blockage) and 1 (no rigidification) [11b].

As another example, Gheimasi et al. recently proposed an optimized procedure in order to simultaneously consider both the partial pore blockage and polymer chain rigidification effects on permeation properties of MMMs using different MMM models. Optimized α and β values can be obtained when a minimized average absolute relative error (*%AARE*) between the experimental data and the predicted values (Eq. (6)) is reached. Such two important parameters P_d and l_I are, however, still arbitrarily assumed [9].

$$\%AARE = \frac{100}{NDP}\sum_{i=1}^{NDP}\left|\frac{P_i^{cal} - P_i^{\exp}}{P_i^{\exp}}\right| \tag{6}$$

here NDP is the number of data points. P_i^{cal} and $P_i^{\exp}$ are the predicted and experimental permeability values, respectively.

In another recent work, Hashemifard et al. developed a model assuming a simple geometrical (non-spherical) shape for the pseudo phase, which involved four independent parameters, namely ϕ_d, $\theta=l_I/2r_d$, $\lambda_d=P_d/P_c$, and $\lambda_i=P_i/P_c$ [10d]. Here, P_i is the permeability of the interfacial phase. The objective function minimized was also *%AARE* (Eq. (6)). For practical predictions, however, a priori assumptions on the type of defective interface are made. For each hypothesized type, arbitrary values are