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The effect of flake orientational order on the permeability of barrier membranes: numerical simulations and predictive models

Marco Dondero, J. Pablo Tomba, Adrián P. Cisilino*

Instituto de Tecnología y Ciencia de Materiales, Facultad de Ingeniería, CONICET, Universidad Nacional de Mar del Plata, Av. Juan B. Justo 4302, B7608 FDQ, Mar del Plata, Argentina

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ABSTRACT

This work presents results of numerical simulations along with the development of simple analytical forms aimed at predicting diffusivity in barrier membranes with randomly dispersed flakes. Simulations are performed using Boundary Element models of representative volume elements that account for the barrier microstructures with high level of detail. Microstructural features such as flake aspect ratio (α) and volume fraction (ϕ) are varied in the range of practical interest ($0.1 \le \alpha\phi \le 5$). Numerical simulations also address the effects of the flake orientational order. Simulation results are used to develop a new model that predicts the elements of the diffusivity matrix as a function of flake arrangement. The basic idea behind the proposed model is to assimilate the parameter proposed by Bharadwaj to describe flake orientational order into the diffusivity model by Lape, which was originally developed for uniformly oriented flakes. The model predictions are shown to be consistent with theoretical limiting behaviors and with those of other models in the literature. The proposed model is among the few ones that accounts for the disorder in the flake orientation, which is found to have a noticeable impact on diffusivity in the direction parallel to the flake orientation.

1. Introduction

The control of barrier properties is relevant to many technologies as a key factor to guarantee product preservation or to protect parts and objects of everyday use from the environment. Beverage bottling, food packaging, protective coatings of diverse nature or drug delivery devices are some of the many application niches that require a fine control of mass transport of gas or liquid species through the material. A useful approach to produce materials with enhanced barrier properties is the dispersion of impermeable elongated objects in a host matrix. The idea behind is that the obstacles increase the path length of the penetrating species so retarding mass transport [1]. This concept has been implemented in polymer based materials with the inclusion of elongated obstacles with lateral dimensions in the nanometric scale (polymer nano-composites). For instance, it has been shown that the incorporation of small amounts of layered silicates (clays) or natural fibers such as cellulose into a variety of polymer matrices produces a remarkable improvement in gas barrier properties.

The prediction of barrier properties like diffusivity, D, or permeability, P, in composite materials is of obvious interest, particularly from the point of view of material design. In other families of barrier materials, such as those composed by multilayers, overall permeability is dictated by a simple combination of properties of the individual layers. In nanocomposites, predictions of barrier properties are certainly more complex as there are several structural features that come into play. For instance, characteristics of the obstacles such as length-to-thickness ratio, α, volume fraction, ϕ, orientation and state of aggregation are expected to affect the overall transport behavior of the composite system. Moreover, in real materials, these variables may not have spatial homogeneity thus adding another level of complexity in the problem description. For example, in the production of parts by injection, extrusion or blown-molding of polymer nanocomposites, shear induced orientation of the nanoclay is unavoidable and it leads to fairly complex orientation patterns of the objects when going from the skin of the part to its core [2].

Some remarkable efforts have been made in the past to understand the effect of α and ϕ of either regular or randomly placed diffusion flakes on overall P or D. The upper bound for diffusivity is predicted by the Voigt's parallel model, which states that for flakes oriented parallel to the concentration gradient, diffusivity decreases, irrespectively of α, in direct proportion with the increase of ϕ. Any other configuration yields lower diffusivities; in particular, models that consider flakes oriented perpendicular to the

* Corresponding author.
E-mail address: cisilino@fi.mdp.edu.ar (A.P. Cisilino).

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concentration gradient predict the minimum diffusivities. These models idealize the penetrant trajectory as a one-dimensional path that experiments abrupt changes in direction when it encounters an obstacle. Thus, tortuous paths retard the penetrant diffusion. The barrier performance can be described in terms of the product $\alpha\phi$, a measure of the mean overall resistance to the diffusion of the penetrant. Models predict two ranges of barrier performance. In the *diluted* limit ($\alpha\phi \ll 1$), D scales with the inverse of the product $\alpha\phi$; obstacles essentially behave independently of each other and the reduction in diffusivity is mostly due to the tortuosity effect [3]. In the so-called *semi-diluted* regime ($\alpha\phi$ close or above 1), D turns out depending on the square inverse of $\alpha\phi$ [1]. As obstacles come closer to each other, the area available for diffusion decreases, further reducing diffusivity. The *semi-diluted* regime is of practical interest as in most of the applications $\phi \approx 0.05$ and $\alpha > 20$, which implies $\alpha\phi > 1$. Other important microstructural factors have also been considered. For instance, Lape et al. [1] assessed the influence of flake aspect-ratio polydispersity on the permeability for the case of flakes oriented perpendicular to the concentration gradient. They concluded that polydisperse flakes have superior barrier properties than monodisperse ones.

Flake orientation with respect to the concentration gradient i.e. aligned or perpendicular, have a profound effect on D. Accordingly, the dispersion of the flake orientation angles is another important aspect to be addressed, as the increase in angle dispersion eventually leads to microstructures with randomly oriented flakes. Fredrickson and Bicerano [4] demonstrated that flakes perpendicular to the concentration gradient are three times more effective in permeability reduction than those with randomly oriented obstacles. Bharadwaj [5] described the dispersion in the orientation angle (orientational order) through the introduction of the order parameter S, derived from liquid crystals theory [6]. Bharadwaj's model predicts that small obstacles are more sensitive to orientational disorder than large ones, although that claim is limited to the diluted limit used for the author as the base of derivation.

High performance numerical tools such as Boundary Element (BEM) and Finite Element (FEM) Methods have taken advantage of the continuous increases in computational power to address the rigorous modeling of complex material microstructures. BEM can solve the diffusion of the penetrant through intricate flake arrangements with high level of detail and accuracy. At the same time, BEM simplifies the problem data preparation and discretization, which is limited to the model boundary [7]. Results of numerical simulations are very useful to obtain further insights on how microstructural features such as flake size, shape and orientation influence on D, beyond the information obtained from the analysis of idealized simple microstructures. Rigorous computer simulations provide a platform of data generation, comparable to those one would obtain from experiments with controlled and well-defined sample geometries.

This work presents the results of a systematic 2D BEM homogenization analyses for the computation of the overall anisotropic diffusivity matrix of flake-filled barrier membranes. The analyses consider microstructures with randomly placed flakes, the size and aspect ratios of which are within the range $0.1 < \alpha\phi < 5$. The homogenization analyses address the effects of the variability of the flake orientation angles, which are characterized via the above referred orientational order parameter, S. Our primary objective is to reduce the simulation results to simple and manageable analytical forms, able to quantitative predict the diffusivity reductions in terms of α, ϕ and S. The paper is organized as follows: we start presenting relevant details of BEM implementation and the results of the numerical simulations. Then, we briefly review some of the relevant analytical models used to predict diffusivity, which will serve as a platform for our further developments. In the subsequent section, we develop a new analytical model that predicts the overall anisotropic diffusivity matrix of the barrier material. The last section discusses some examples that highlight the capabilities of this new model.

2. Problem description

The analysis addresses the two-dimensional diffusion of a solute through flake-filled membranes, like the ones depicted in Fig. 1. The matrix material is homogeneous and isotropic, whereas the flakes are of rectangular shape and they are impermeable to the diffusing species. Dimensions of the flakes are $2a \times b$ with $a > b$ (see Fig. 2a). The membrane microstructure is described in terms of the flake volume fraction $\phi = A_{flakes}/A_{membrane} = \frac{n(2a \times b)}{L \times W}$, where n is the number of flakes and L and W are the membrane length and width, respectively. The flake aspect ratio is defined as $\alpha = a/b$. The flake orientation is described in terms of the mean orientation angle $\bar{\theta}$ and its standard normal dispersion σ.

Fick's second law governs the diffusion of the solute through the membrane matrix. At the steady state, the conservation of the solute mass implies,

$$\nabla \bullet \mathbf{q} = 0, \tag{1}$$

where $\mathbf{q}$ is the diffusion flux. The constitutive equation for the flux is

$$\mathbf{q} = -D\nabla\varphi, \tag{2}$$

where φ is the solute concentration and D is the diffusion coefficient of the neat matrix, which is assumed to be not affected by the presence of the flakes. The symbol ∇ stands for the gradient operator. Bold letters indicate vectors and matrices. Vector components are indicated with subscripts; for instance q_1 and q_2 indicate the fluxes in the directions along and across the membrane, respectively.

Due to the presence of flakes, the membrane is anisotropic in terms of diffusion properties. The respective diffusivity matrix is

$$\mathcal{D} = \begin{bmatrix} \mathcal{D}_{11} & \mathcal{D}_{12} \\ \mathcal{D}_{21} & \mathcal{D}_{22} \end{bmatrix}, \tag{3}$$

where the $\mathcal{D}_{ij}$ components are the diffusivities associated to the flux in the i-direction due to a concentration gradient in the j-direction.

Matrix $\mathcal{D}$ is a second-order tensor, so it can be rotated using the well-known rotation formula

$$\mathcal{D}' = \mathbf{R}\mathcal{D}\mathbf{R}^T = \begin{bmatrix} \cos(\theta) & -\sin(\theta) \\ \sin(\theta) & \cos(\theta) \end{bmatrix} \begin{bmatrix} \mathcal{D}_{11} & \mathcal{D}_{12} \\ \mathcal{D}_{21} & \mathcal{D}_{22} \end{bmatrix} \begin{bmatrix} \cos(\theta) & \sin(\theta) \\ -\sin(\theta) & \cos(\theta) \end{bmatrix}, \tag{4}$$

where θ is the rotation angle.

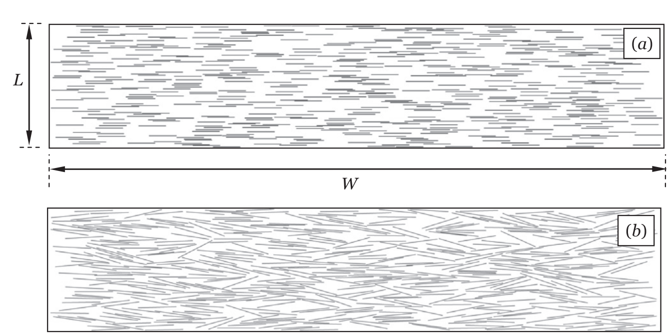

Fig. 1. Geometries of typical models of the membrane microstructures: $\phi = 0.1$, $n = 500$, $\alpha = 25$, orientation angle $\bar{\theta} = 0°$ with normal dispersion (a) $\sigma = 0°$ and (b) $\sigma = 10°$.