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A comprehensive model for mass transport properties in nanocomposites

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ABSTRACT

Relations between morphological characteristics and effective permeability in nanocomposite systems are here considered in details, both analyzing modeling results for simple systems as obtained in different past attempts and extending the applicability of the latter to more realistic configurations.

In this perspective, the same mathematical tool and modeling approach used in a previous paper for the analysis of simple 2-D ordered systems [J. Membr. Sci. 327 (2009) 208–215] are here extended in several different respects. Predictions from numerical simulations for 3-D ordered and random systems, both for the case of low and high concentration of inclusions, are compared with results from previous works and with correlations offered by empirical approaches. A new model is finally proposed for the prediction of permeability in random systems which proves to be reliable in a rather large range of geometrical and morphological configuration.

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1. Introduction

In the last decades, thin films of composite materials obtained through fine dispersion of an inorganic phase into a polymeric matrix have been widely investigated in view of the possibility of controlling film properties. Indeed, remarkable improvements of film performance were obtained in several cases through the addition of just few percents by weight of inorganic filler [1–7]. In particular, it has been shown that, together with improvements in mechanical strength and thermal stability, the addition of high aspect ratio inorganic platelets to a polymeric material can definitely increase its barrier properties to gases and vapors [7,8].

In this concern, several works have been devoted to modeling and simulating the diffusion in heterogeneous media, aimed to relate the barrier effect to the structural properties of the nanocomposite material. Both analytical and numerical approaches were considered to study this phenomenon at different levels of approximation, in addressing the complexity of domain geometry [9–16].

In a previous work [17], a CFD technique, based on a finite volume algorithm, was employed to simulate the gas transport process in a polymeric phase filled by an impermeable moiety regularly dispersed into the matrix. The proposed method was focused on representing the effect of tortuousity on the path-line of diffusing species, as induced by the presence of impermeable particles. Limited to the case of 2-D geometry, ordered structures were analyzed to show both suitability and reliability of such technique through a review of mathematical models already proposed in the literature for the description of similar barrier effect [11–13,18,19].

It has been shown in the previous work [17] that the most frequently cited model equation attributed to Aris, is reported erroneously in the original paper [11], leading to incorrect formulations of several predictive equations derived from that. A model build after the correct Aris's equation was then presented, and ability of the latter to predict numerical results obtained for diffusion in 2-D ordered nanocomposites has been showed [17].

Such model, however, is of limited use in analysis of experimental data, due to the assumption of two-dimensional perfectly ordered geometry, which poorly compares with real structures. In fact, in real nanocomposites, the filler is randomly dispersed into the matrix, no order can be found and some of the ordered model parameters cannot be measured, or even precisely defined, because of the lack of physical meaning. A more general analysis is thus needed in order to obtain a model suitable for the discussion of properties of the real materials.

The present work addresses the description of mass transport properties in systems with randomly dispersed impermeable flakes, adapting to this rather general structures the finite volume approach already developed for 2-D ordered geometries. The aim is to obtain relevant information on structure-properties relationships of such materials. The model must necessarily first address the 3-D nature of real systems geometry.

Three-dimensional approaches for the description of 3-D systems have already been attempted [15,20,21] and many efforts have been devoted to simulations [22] and numerical calculations [23] to produce and validate empirical relationships for the prediction of the enhancement in barrier properties.

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After a brief discussion of existing models, the first part of this work will consider generalization of results obtained in the previous work [17] to the case of 3-D ordered nanocomposite systems. In the second part of the study, 2-D and 3-D random geometries are considered to fully understand the implications involved in the extension of this geometrical approach from ordered to random systems. The results obtained by numerical calculations performed for several different configurations will be presented and discussed. A simple relation will be finally proposed which allows for the analysis of experimental data in terms of relevant structure characteristics.

2. Transport problems examined and numerical simulations

2.1. Numerical simulations

In the present work, a continuous model is used to describe the diffusion process in flake filled systems for the case in which flakes are impermeable to penetrant species.

Briefly, the steady state diffusion process of a single penetrant species in the two-phase medium is governed by Fick's law, which is assumed to hold at all points in the continuous permeable isotropic phase with uniform diffusivity:

$$\underline{J} = -D_0 \cdot (\underline{\nabla} c) \tag{1a}$$

$$0 = \underline{\nabla} \cdot \underline{J} \tag{1b}$$

The description of the problem is then completed by assigning the values of concentration at inlet and outlet boundaries of the system domain and imposing a null value of mass flux across the interface (normal vector $\underline{n}$) between permeable phase and impermeable platelets:

$$0 = (\underline{\nabla} c) \cdot \underline{n} \tag{2}$$

Upstream and downstream surfaces parallel to flake planes, characterized by different uniform values of penetrant concentration, were considered as inlet and outlet boundaries in all calculations. In this analysis, indeed, only the case of effective penetrant mass flux directed normal to flake planes in the nanocomposite systems is addressed.

The numerical solution of the problem was finally approached by discretizing the computational domain and solving Eq. (6) with the control volume technique [24].

Results from the simulations are finally reported as ratio between permeability of pure continuous phase and corresponding effective values computed for the composite system. The latter quantity is here indicated as D_0/D_{ff}, resembling notation used in several works already published on the same subject, with reference to pure continuous phase diffusivity, D_0, and corresponding effective value D_{ff} for flake filled system.

The results from numerical solution for the case of 2-D structures with an ordered distribution of flakes were reported and discussed in a previous paper [17]. In the present work, the same approach is applied to the analysis of different types of geometries. Results obtained for 3-D ordered geometries are first discussed, considering the case of different shapes for the flake cross section. Decrease of diffusion rate in a medium obtained through random distribution of impermeable platelets is then considered and results are compared as obtained for circular or squared flakes in 3-D domains and for simpler 2-D geometries.

2.2. Numerical calculations for 3-D ordered structures

All types of 3-D ordered configurations considered in this work are shown in Fig. 1, in which flake arrangements are represented as they appear in direction normal to flake planes and in solid lines are represented borders of flakes that lie on the same layer. Ordered structures made by flakes in shape of square tablet (Fig. 1a), hexagonal tablet (Fig. 1b), octagonal tablet (Fig. 1c) and circular disc (Fig. 1d) have been considered. Flake filled 3-D ordered structures can be obtained in several different ways, even when reference is done to the same flake shape, and a precise description of their spatial arrangement is therefore necessary to allow for a meaningful comparison with different analysis or calculation results. In the present case, only few simple planes arrangements are considered and are represented in Fig. 1. The different geometries could also be described by using standard notation for crystallography. Systems here considered for flakes in square or octagonal tablets shape can be described as their central points were ordered in a body centered cubic (bcc) arrangement for which flake planes correspond to Miller index (1 0 0), while configuration for flakes in circular discs or hexagonal tablets shape may be described by a face centered cubic (fcc) lattice with flake planes oriented as indicated by Miller index (1 1 1).

It should then be noted that the structures studied in this work are similar, but not coincident, with those considered in other works [22,23] and these differences must be taken into account for a proper comparison of simulation results.

With reference to a generic configuration built after platelets of different shapes, a unique definition of geometry parameters, "flake aspect ratio" α and "slit shape" σ, which are usually considered to describe such systems, is here proposed as follows:

$$\alpha = \frac{S_n}{S_L} \tag{3}$$

$$\sigma = \frac{S_{n,\mathrm{H}}}{S_L} \tag{4}$$

where S_n and $S_{n,\mathrm{H}}$ are the cross section areas for flake cross section (normal to the flux direction) and for hole region, respectively, on the flakes plane, while S_L is the area of the flake lateral surface.

The parameter α somehow measures the relative maximum extension of penetrant molecule path-line when circumventing a single flake. Parameter σ/α, on the other hand, measures the relative probability of free pass/flake impact events for the single molecule when crossing a single flake layer.

The set of parameters here used to describe the system geometry is completed by the loading ϕ, defined as the volume fraction of flakes in the system.

Above definitions are consistent with those given in previous works [17] for 2-D geometries, and will be used for all comparisons among the present results and those available in the literature, although a particular care should be devoted in accounting for differences with respect to definitions given for aspect ratio and slit shape in other works. It should be noted that parameters α and σ defined above only refer to single flake plane geometry and thus no account is given, through the parameters set here used, of the specific planes arrangement in the ordered nanocomposite system.

In numerical analysis, a wide range of aspect ratios has been investigated, from 5 to 300, with loadings between 0.5% and 10%. Slit shape was also varied between 0.5 and 5. In this concern, it should be noted that only for the case of flakes shaped in squares or hexagonal tablets arbitrarily low values for the parameter σ/α can be reached, while for the case of flakes shaped in circular discs and octagonal tablets, the definition of the slit shape given in Eq. (4) results in non negligible values of σ even at close-packing conditions for the single flakes plane.

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