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Numerical simulation and mathematical modeling of 2D multi-scale diffusion in lamellar nanocomposite

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ABSTRACT

In this work, FE analysis was used to study steady-state diffusion into 2D polymer nanocomposites. The developed FE model is made of randomly distributed and randomly oriented permeable lamellar stacks made of a certain number of platelets, separated by galleries. The model is able to account for diffusion occurring between lamellar stacks, as well as within stacks, inside lamellar galleries. This allows to account for different morphologic features of the nanofiller, including the number of lamellae in each stack, which defines the degree of dispersion, and the lamellar gallery thickness, indicative of the degree of intercalation. Simulation results showed that the normalized coefficient of diffusion only depends on the normalized path length, which is, in turn, dependent on the morphology of the nanocomposite. Besides the aspect ratio and volume fraction of the nanofiller, also the degree of intercalation and the degree of dispersion play a significant role in determining the barrier properties of nanocomposites.

The behavior of nanocomposites made of permeable lamellar stacks was represented by introducing a geometrical model, which is based on the probability of collision of diffusing particles on the lamellar surface. For a random orientation of lamellar stacks, the developed model showed an excellent agreement with the simulation results. The developed model also allowed to estimate the error arising from the assumption of impermeable stacks when using permeability data in order to calculate the aspect ratio of nanofillers.

1. Introduction

Gas permeability improvement is one of the most promising application of mono-dimensional (1D), platelet shaped, nanofillers dispersed in a polymeric matrix [1–5]. It is generally recognized that the barrier properties of polymer nanocomposites mainly depend on volume fraction, orientation and aspect ratio (i.e. ratio between the lateral dimension and the thickness of a stack of nanoplatelets) of the nanofiller [2,6–10]. The aspect ratio is strongly dependent either on the degree of dispersion either on the degree of intercalation of the nanofiller. As formerly reported for lamellar silicates [5], dispersion and intercalation define two different morphologic properties of the nanocomposite. In facts, the former depends on the number of platelets which are, on the average, present in each single stack, whereas the latter defines the thickness of lamellar galleries, the spacings between nanofiller platelets. When dealing with completely exfoliated lamellar silicates, the two concepts can be considered equivalent. Each stack is composed of a single platelet (complete dispersion) and the thickness of lamellar galleries cannot be anymore measured. In such cases, the aspect ratio of the nanofiller can be reasonably assumed to be equal to the aspect ratio of nanofiller platelets. On the other hand, looking at the morphology of an intercalated nanocomposite, different situations can arise. It is possible to have a strongly intercalated, weakly dispersed nanocomposite, in which, despite the high thickness of galleries, each stack is composed of many platelets. On the opposite, a strongly dispersed, weakly intercalated nanocomposite can be formed when lamellar galleries keep their original size, but the stacks are composed of a few number of platelets. This is the case, for example, of nanocomposites obtained using graphene oxide (GO), which are processed aiming to obtain a good degree of dispersion, since intercalation is hardly to be achieved, due to the very thin lamellar galleries [11].

Gas permeation in intercalated polymer nanocomposites should be considered at two different scales [12]: the first one is associated with diffusion between stacks, and the second one is associated to diffusion inside lamellar galleries. This kind of problem has been studied in other research fields, as for example in the analysis of polymer flow during fiber impregnation. In such cases it has been recognized that two mechanisms of impregnation, each characterized by a proper value of permeability, occur, the first one

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defined as macro-impregnation, and the second one defined as micro-impregnation [13]. Diffusion in polymer nanocomposites characterized by an intercalated morphology can follow a similar path, since diffusion can occur either between lamellar stacks, either inside stacks, i.e. through the lamellar galleries. In this case it would be possible to define an inter-stack diffusion and an intra-stack diffusion.

Therefore, the aim of this paper is to study the 2-D diffusion behavior of intercalated nanocomposites by FE analysis. Compared to other works reported in literature, the present work for the first time introduces a geometric model which is also able to account for permeability of lamellar stacks. To this purpose, a Matlab routine formerly developed for impermeable stacks or completely exfoliated nanocomposites [14,15], was modified in order to account for diffusion inside lamellar galleries. The routine is able to produce a random array of non-interpenetrating, randomly oriented, stacks, each composed of a given number of platelets, separated by lamellar galleries of arbitrary thickness. To the best of our knowledge, this is the first time that such a mesoscale approach is introduced to study diffusion in polymer nanocomposites. In order to analyze the simulation results, a geometrical model was developed, which is able to predict the evolution of normalized path length as a function of nanocomposite morphological properties, including degree of dispersion and intercalation.

2. Simulation of diffusion in nanocomposite

Diffusion in nanocomposites made of permeable stacks of platelets was studied using the finite element (FE) Comsol Multiphysics software (version 3.5, Comsol AB, Sweden). 2D geometry was adopted, modeling the nanocomposite as an array of stacks uniformly and randomly dispersed in the square integration domain, characterized by an edge length L_0. The position and orientation of stacks inside the domain was randomized by means of a properly developed subroutine of Matlab 6.5, based on a Monte Carlo stochastic approach. The program includes non-interpenetration conditions between stacks.

A sketch of a typical domain obtained following this procedure is reported in Fig. 1.

As it can be observed, each stack is composed by a regular arrangement of parallel and equidistant platelets separated by galleries. Randomization only affects the position and orientation of stacks. The domain is composed of "external" boundaries, which are the external contour of the domain, and "internal" boundaries, which are the interface between the platelets and the intercalated polymer. In the simulations, it is assumed that the coefficient of diffusion inside galleries (intra-stack diffusion) is the same as the coefficient of diffusion between stacks (inter-stack diffusion).

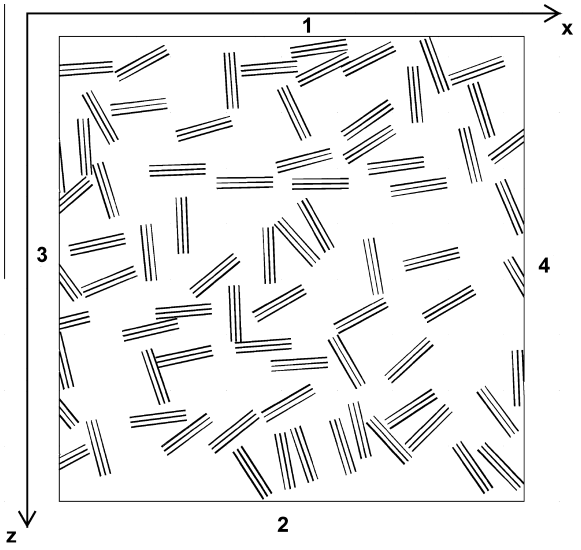

Fig. 1. Integration domain in 2D geometry.

The problem is solved by means of the Mass Transport module, Diffusion sub-module, in stationary conditions, which assumes the mass balance equation:

$$\nabla^2 c = 0 \tag{1}$$

coupled with the proper boundary conditions:

$$\frac{\partial c}{\partial n} = 0 \text{ at each platelet surface with normal } n \text{ (impermeability)}; \tag{2}$$

$$\frac{\partial c}{\partial n} = 0 \text{ at the boundaries of the domain (lines 3 and 4 in Fig. 1a) parallel to the direction of diffusion } (z \text{ axis}); \tag{3}$$

$$c = c_1 \text{ at the upper boundary of the domain perpendicular to the direction of diffusion;} \tag{4}$$

$$c = 0 \text{ at the lower boundary of the domain perpendicular to the direction of diffusion.} \tag{5}$$

The concentration c_1 was chosen in order to have, for all the simulations, a concentration gradient $\frac{c_1}{L_0} = 1E3$.

The Matlab routine also includes a subroutine for the calculation of the average path of massless particles diffusing due to concentration gradient [14]. The normalized path, L_{norm}, was obtained as the ratio between the average path of diffusing particles inside the nanocomposite and the length of the domain in the direction of diffusion, i.e. L_0, which corresponds to the direct diffusion path in absence of lamellae.

The coefficient of diffusion of the nanocomposite was obtained as the average value of the normal flux on the two boundaries perpendicular to the direction of diffusion, divided by the concentration gradient. The normalized diffusion coefficient, D_{norm}, was obtained as the ratio between simulated coefficient of diffusion of the nanocomposite and matrix diffusivity.

Simulations were run at two different volume fractions v_f (0.015 and 0.03) and aspect ratio of platelets, AR_L (100 and 50). For each value of volume fraction and platelet aspect ratio, different simulation were run, changing the morphology of the nanocomposites, including the number of platelets in each stack and the lamellar gallery thickness. A sketch of the geometric features of each stack is reported in Fig. 2.

The stacks are characterized by the width W, the number of platelets, N_L, each of thickness T_L, and the number of galleries $N_G = N_L - 1$, each of thickness T_G. The total thickness of the stack is T_S:

$$T_S = N_L T_L + (N_L - 1) T_G \tag{6}$$

The two parameters which determine the morphology of the stack are the number of platelets in each stack, indicative of the degree of dispersion, and the thickness of the galleries, indicative of the degree of intercalation [5]. According to the scheme of Fig. 2, the aspect ratio of the platelets is defined as:

$$AR_L = \frac{W}{T_L} \tag{7}$$

whereas the aspect ratio of the stack can be obtained by Eq. (6) as:

$$AR_S = AR_L \frac{1}{N_L + (N_L - 1)\frac{T_G}{T_L}} \tag{8}$$