Computational Materials Science 83 (2014) 164–170

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Simulation and modeling of diffusion in oriented lamellar nanocomposites

A. Greco *

Department of Engineering for Innovation, University of Salento, Via per Monteroni, 73100 Lecce, Italy

ARTICLE INFO

Article history:
Received 18 September 2013
Received in revised form 31 October 2013
Accepted 5 November 2013
Available online 1 December 2013

Keywords:
Nanocomposite
Diffusion
Modeling
Simulation
Orientation

ABSTRACT

In this work, diffusion in oriented lamellar nanocomposites was studied by means of FEM analysis. The developed FEM model, based on a random distribution of non-interpenetrating impermeable lamellae with arbitrary orientation, was used to calculate the coefficient of diffusion in lamellar nanocomposites in 3D and in 2D diffusion, at different values of filler volume fractions, aspect ratio and orientation angles. Comparison between coefficient of diffusion obtained by simulation results and Bharadwaj model showed a good agreement. Nevertheless, it was found that the good agreement derives from two counteracting errors, balancing their effect: overestimation of the diffusion length and underestimation of the dependence of normalized diffusion coefficient upon normalized diffusion length. Therefore, in order to gain a better understanding of the diffusion in lamellar nanocomposites, an analytical model was developed, which is able to predict the evolution of coefficient of diffusion as a function of orientation, volume fraction and aspect ratio of the nanofiller.

The comparison between the simulation results and analytical model showed a very good agreement, comparable to that found for the Bharadwaj model. In addition, the developed analytical model provided an excellently good estimation of the diffusion length.

1. Introduction

In the last decades, fine dispersions of an inorganic phase into a polymeric matrix, usually referred to as nanocomposites, have been widely investigated in view of the possibility to control material properties. The addition of a few percent of monodimensional, platelet shaped, nanofiller, has shown a potential in order to reduce the diffusion coefficient of gases inside the polymer [1–5]. The enhanced barrier properties of nanocomposites compared to the neat matrix is attributed to the increase of tortuosity, which is defined as the ratio between the path that a diffusing particle runs in the nanocomposite and the path run in the absence of nanofiller [3,4,6].

Besides experimental measurements of their permeability, the research in the field of polymer nanocomposites is focused either on numerical simulation [7–11] or on analytical modeling [10–16]. The problem of diffusion has been studied by finite element analysis, considering different levels of approximation to the real nanocomposite nanostructures, starting form regularly spaced, parallel flakes in 2D [7] or 3D [8] geometries, to random distributions of perfectly aligned flakes [9]. Such simulations, however, only consider platelets oriented perpendicular to the direction of diffusion, which represents the higher efficiency in barrier properties enhancement, and are hardly encountered in most practical applications. Only recently, the effect of orientation of nanoparticles towards the direction of diffusion has been introduced in 2D [17] and 3D [12] geometries. Mathematical modeling of diffusion in polymer nanocomposites has also gained a relevant interest in order to correlate the experimental values of diffusivity to the morphological features of the nanocomposite. As in the case of finite element analysis, the problem of diffusion is studied at different levels of approximation of real nanocomposites structures, and in most cases the analytical models proposed in the literature deal with particular cases of nanoparticles perfectly aligned perpendicularly to the direction of diffusion. Recently, a model has been developed, which is able to predict the behavior of randomly oriented nanoparticles in 2D and 3D geometries [12]. Nevertheless, the only model which is able to capture the effect of the orientation on the diffusion behavior of nanocomposites was developed by Bharadwaj [15], which coupled the tortuosity factor introduced by Nielsen for particles perfectly aligned perpendicular to the direction of diffusion [18] with the definition of an order parameter, commonly used to represent the orientation factor in liquid crystalline structures [19].

Therefore, the aim of this paper is the analysis of diffusion in 2D and 3D nanocomposites with different orientation of lamellae. Diffusion was initially studied by FE analysis, through a geometric

* Tel.: +39 832 297233.
E-mail address: antonio.greco@unisalento.it

0927-0256/$ - see front matter
http://dx.doi.org/10.1016/j.commatsci.2013.11.019

model including an array of rectangular or disc shaped lamellae. An analytical model was derived, aiming to predict the diffusion coefficient and diffusion length of nanocomposites with oriented platelets. Comparison with simulation data showed an excellently good agreement, comparable to that obtained by the Bharadwaj model.

2. Simulation of diffusion in oriented nanocomposite

The FE model used in this work has been derived from that introduced in a previous work, devoted to study diffusion in randomly oriented nanocomposites [12]. Both 2D and 3D geometries were adopted, modeling the nanocomposite as an array of impermeable platelets uniformly and randomly dispersed in the domain, which behaves as a Fickian medium. In 2D simulations, a squared domain was used (edge length L_0) and platelets were represented by means of rectangles of width W, and thickness T, characterized by an aspect ratio given as W/T. In 3D simulation, a cubic domain was used (edge length L_0), and platelets were represented as discs of diameter W and thickness T, characterized by an aspect ratio W/T. The position of lamellae inside the domain was randomized by means of a subroutine properly developed in Matlab 7.8, which, through a Monte Carlo stochastic approach, produces random numbers and provides as an output a file that contains the centers of uniformly and randomly dispersed platelets. The program includes noninterpenetrating conditions between platelets.

A very relevant feature, significantly influencing the diffusion behavior of nanocomposites, is the orientation angle of nanoparticles. In 2D simulations the orientation angle is simply defined as the angle enclosed between the normal vector to the platelet surface and the direction of diffusion. In 3D, completely defining the orientation of each platelet would require two orientation angles: θ, which is the angle formed between the direction of diffusion and normal vector to the platelet surface, and α, which defines the rotation of the normal vector about the z axis, or the rotation in the x–y plane [20]. On the other hand, for disc shaped platelets, it is expected that rotation in the x–y plane does not influence the diffusion trough the nanocomposite [21]. As a consequence, solely the angle θ determines the barrier properties of nanocomposites, and is therefore considered as the effective orientation angle.

In a previous work [12], it was shown that FE modeling provides the same results for the coefficient of diffusion either if nanoplatelets are characterized by a distribution of orientation angle, or if nanoplatelets are characterized by a fixed value of the orientation angle. Therefore, for the sake of simplicity, each simulation was run using a fixed value of the orientation angle, equal for all the platelets in the domain. On the other hand, since the orientation angle is defined as the absolute value of angle formed between the normal to the platelet surface and the direction of diffusion, the sign of the orientation angle was also randomized.

A sketch of the domains obtained in 2D and 3D are reported in Fig. 1a and b. The Matlab subroutine also includes a noninterpenetrating condition between each platelet and the boundaries perpendicular to the direction of diffusion (lines 1 and 2 in Fig. 1a).

Finite element (FE) solutions were obtained by using the Comsol Multiphysics software (version 3.5, Comsol AB, Sweden). The problem is solved by means of the Mass Transport module, Diffusion sub-module, in stationary conditions. The software, assuming a uniform diffusivity of the diffusing species in the polymer domain, solves the mass balance equation:

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

coupled with the proper boundary conditions:

$$\frac{\partial c}{\partial n} = 0 \tag{2}$$

at each lamella surface boundary with normal n (impermeability);

$$\frac{\partial c}{\partial n} = 0 \tag{3}$$

at the boundaries of the domain (lines 3 and 4 in Fig. 1a) parallel to the direction of diffusion (z axis);

$$c = c_1 \tag{4}$$

at the upper boundary of the domain perpendicular to the direction of diffusion (line 1 in Fig. 1a);

$$c = 0 \tag{5}$$

at the lower boundary of the domain perpendicular to the direction of diffusion (line 2 in Fig. 1a).

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

Comsol postprocessing results included the calculation of the length of the diffusion path of massless particles [12]. 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 the neat matrix. The coefficient of diffusion of the nanocomposite was obtained as the average value of the normal flux on the two boundaries perpendicular to the

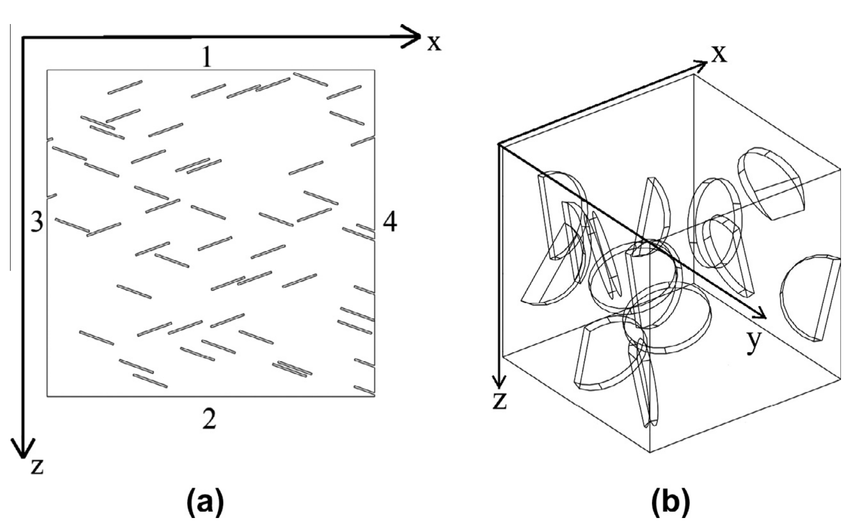

Fig. 1. FEM simulation domains in 2D (a) and 3D (b).