A 3-D APPROACH TO MODEL DIFFUSION IN RANDOMLY DISTRIBUTED NANOCOMPOSITE

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Abstract

The mass transport properties of a system with impermeable platelets dispersed in a polymer matrix were investigated, through a numerical algorithm, based on finite volume method. Simulations were carried out on 3-D geometries where different shapes of the lamellae were considered, dispersed in both an ordered and random way; different volume fractions ϕ and aspect ratios α of the platelets were considered, and, in the ordered structures, also different values of the flakes spacing σ were investigated. In the case of random systems, multiple structures were analyzed for a given set of parameters and the results were treated statistically to obtain reliable information.

The results show that the permeability in ordered geometries decreases with the product $\alpha\,\phi$ and that the curves corresponding to different filler shapes have a similar qualitative behavior but quantitative differences in the enhancements of the material barrier properties; circular platelets in particular, showed to be less efficient than other geometries in decreasing the effective diffusivity of the composite. All 3-D structures then showed diminished barrier properties with respect to homologous 2-D structures suggesting that the use of the latter approach would lead to an overestimation of the barrier properties increases in real nanocomposites and thus, despite its simplicity, should not be used for this purpose.

The data relative to 3-D random dispersions, that show barrier properties even worse than those of ordered dispersions of circular lamellae, can be accurately predicted by the Nielsen's model approach which therefore seems more suitable to describe the properties of real materials.

Introduction

Currently nano-technology are widely investigated due to the interesting properties that have been achieved in the last decades by in terms of the mechanical behavior, flame resistance and barrier properties, just with addition of small amounts of a nano-structured inorganic, impermeable phase in a polymeric matrix [1-3]. Such improvements make these materials suitable for several applications and, the effect on the barrier properties in particular has made such nanocomposite materials very attractive in the field of food packaging.

From this point of view, therefore, the study gas molecules diffusion through these heterogeneous membranes is today regarded with renowned interest; this is indeed a classical problem in the field of the transport phenomena that, although widely studied through analytical and computational approaches, has not been completely understood yet [4-7].

In this work a finite volume based algorithm has been applied to the analysis of ordered and random tri-dimensional structures; the enhancement of the barrier properties was studied in relation to the structural parameters such as the platelet aspect ratio α (the ratio between the half-with of the flake to its thickness), the filler volume concentration, the so-called loading ϕ, and, for the case of ordered geometries, the slit shape σ which represents ratio between the flakes spacing and thickness.

Many works have already been carried out on this problem, but most of them have considered just the case of 2 dimensional structures [6-10] that is only a rough approximation of the real structure which one can find in the real nanocomposites. The aim of this work was therefore to analyze the barrier properties in 3-D geometries, definitely more suitable to describe the real case, in order to reach a better understanding of the relationship betweens structure and properties of such nanocomposites materials.

Simulation details

The process, which has been simulated, is a purely diffusive phenomenon considering small penetrant molecules in a two components medium, where the mass transfer is governed by the Fick's law. The heterogeneous lamellar structure as usually considered in 2-D approach has been transposed in a tri-dimensional space by developing 4 different ordered configurations as shown in Figure 1.a,b,c,d. As one can see squares and circles are considered, as well as the octagons, to mimic the shape of the flakes usually dispersed in a polymeric phase. Tapes-shaped geometries were instead obtained by basically extruding the 2-D lamellae in the third direction and they have been considered to have a direct comparison with the results obtained in the bi-dimensional case.

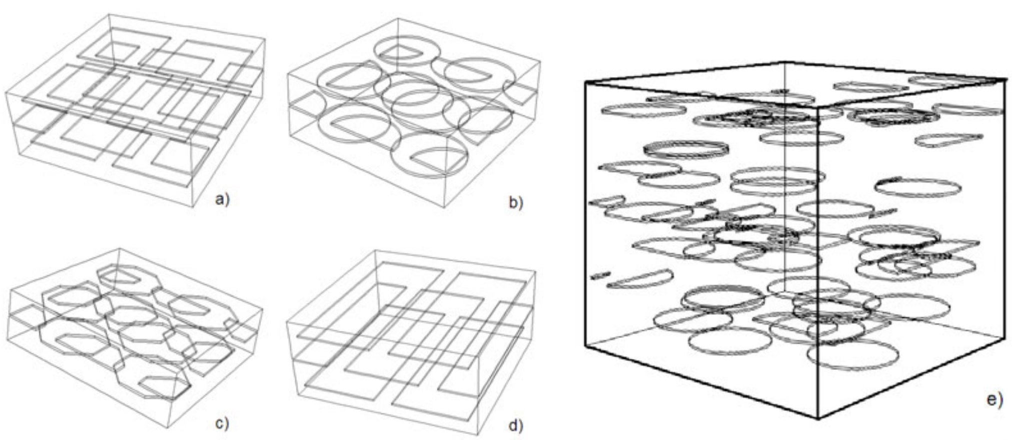

Figure 1, 3-D ordered heterogeneous geometry, squares (a), circles (b), octagons (c) and tapes (d). On the right side the layout of a disordered configuration (e).

These structures are represented by three parameters, as above mentioned, the flakes aspect ratio, the slit shape, and the filler volume fraction whose values have been changed during the simulations in order to investigate all the possible regimes due to the different geometries. In particular the different geometries were built with α values from 20 to 100, slit shapes in the range of 0.01–10, and loading of 0.5 to 20 %. The so-generated structures were then meshed, with a particular care in the critical areas, and the Fick's equation was solved through a finite volume algorithm.

In the case of random systems just circular configuration has been chosen and the geometries were defined by randomly placing a certain number of, not overlapping, platelets in the simulation box. In order to mimic the poly-dispersity of filler dimensions in the real composite the aspect ratio α of the platelets was allowed to vary and a standard deviation of about 10 % of the average value was used to obtain a normal distribution of such parameter in the geometry. In this way, random structures were obtained as the one showed in Figure 1.e. Aspect ratios of 20, 50, 75, 100, as average values, and different filler volume fractions, namely 2.5, 5 and 10 %, were thus considered to investigate the influence of the loading on the composite transport properties.

The same procedure and the same solver were used in case of randomly distributed systems, but, for same set of parameters, simulations were performed on different geometries in order to obtain results independent from the particular structure tested. This procedure was considered to have better statistic on the data and allowed to minimize the standard deviation of the results obtained for a given set of parameters which was indeed kept to a value of about 10 % of the average permeability ratio.

Theoretical background

As previously mentioned the problem of diffusion in a nanocomposite media has been investigated by different authors and different approaches were considered leading to a number of different models proposed both for 2-D and 3-D structure.

In particular, even limiting the analysis to the most interesting models, it should be recalled that one of the first theories in the field was developed by Barrer [11] at first and then modified by Nielsen [12] which proposed the following relationship:

$$\frac{D_0}{D} = 1 + \frac{\alpha\phi}{1-\phi} \qquad (1)$$

where D_0 is the diffusivity through the unfilled material, D is the diffusivity through the nanocomposite membrane and the other symbols have been already introduced.

This model based on ordered 2-D structure was extremely simplified and many authors tried to give more rigorous representation of the barrier effect introduced by filler platelets, this approach lead, among the other, to the following relationship for 2-D ordered structures [9]:

$$\frac{D_0}{D} = 1 + \frac{\alpha^2\phi^2}{1-\phi} + 2\frac{\alpha\phi}{\sigma} \qquad (2)$$

Where the different terms refers to two different types of resistance in the materials: one, linear to the product $\alpha\phi$, was related to the flow constriction in the holes between two adjacent flakes, while the other, of second order with respect to α ϕ, refereed to the tortuous path of the molecule among two different layers of platelets. Such approach was then extended to describe the properties of 2-D and 3-D random systems, in the case of high aspect ratio, obtaining the following equation [13]:

$$\frac{D_0}{D} = 1 + \mu\alpha^2 \frac{\phi^2}{1-\phi} \qquad (3)$$

where a geometrical factor μ, basically dependent on the flake geometrical characteristics, was introduced as a fitting parameter

Other models were then proposed based on numerical analysis (through finite element approach) of the mass transport in nanocomposite materials. In particular in the work due to Gusev, the following formula was presented [14]:

$$\frac{D}{D_0} = \exp\left(-\frac{x}{x_0}\right)^{\beta} \qquad (4)$$

where $x = \alpha\,\phi$ and $\beta = 0.71$ and $x_0 = 3.47$ were basically two fitting parameters calculated in the base of the numerical results.

A second work is instead due to Friedrickson and Bicerano, which, based also on physical considerations, obtained a model of the following form [15]:

$$\frac{D}{D_0} = \frac{1}{4}\left(\frac{1}{1 + a_1\kappa\alpha\phi} + \frac{1}{1 + a_2\kappa\alpha\phi}\right)^2 \qquad (5)$$

where: $a_1 = \left(2 - \sqrt{2}\right)/4$ and $a_2 = \left(2 + \sqrt{2}\right)/4$ and $\kappa = \pi / \ln\alpha$.

Results

Ordered 3D structures

In the present work, the resistance to diffusion in nanocomposite systems was investigated in a wide range of filler concentration and flakes aspect ratios; 4 different configurations of the platelet were also considered to understand the influence of these parameters on the final properties of the materials. The results are presented in Figure 2, that shows the differences between the 4 shapes of platelets in terms of diffusivity ratio as function of α times ϕ; D/D_0, indeed, as most of the authors suggested does not depends on α and ϕ separately but, once the value of σ is defined, is mainly related to their product.

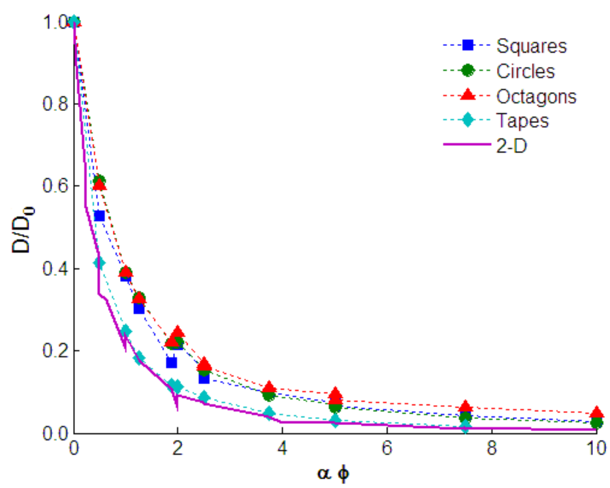

Figure 2, Permeability ratio in ordered systems for the 4 different configurations and the results in 2-D geometries are also reported as comparison. All the geometries are in case of σ=1

In the figure it can be seen that the barrier properties of the material definitely depends on the platelets shape since, for a given set of parameters, the value of D/D_0 ratio results to decrease going from circular flakes, which show lower barrier enhancements, to platelets shaped respectively as octagons, square and tapes. The curve due to the latter geometry then, lies exactly over the results obtained in the 2-D analysis, confirming the internal consistence of the numerical approach, because this configuration has been obtained extending indefinitely the 2-D lamellar geometry in the third direction.

In order to better understand the dependence of the barrier properties as a function of the $\alpha\phi$ product the relative change of diffusivity (D_0/D-1) can be considered. Such parameters which represent a sort of resistance to the diffusion shows a trend that can be approached by a power law with a variable exponent. As shown in Figure 3, indeed, this quantity behaves in two different ways when the entire range of $\alpha\,\phi$ is considered; for diluted systems and small platelets ($\alpha\,\phi$ small) the trend is linear, while increasing $\alpha\,\phi$ the dependence increases and on the right side of the plot becomes approximately quadratic. This behavior closely resemble to what predicted by the simple model for 2-D structured system presented in Eq. 2 so that one can say following the same approach that, also in the case of 3-D ordered system two different behavior are evident, the first valid for low platelet concentration where the resistance is mainly focused in the hole area, while the very few lamellae in the system are not enough to increase significantly the tortuosity of the penetrant path. The second valid for high $\alpha\,\phi$ factor when the "wiggling" of the diffusing molecules between the platelets is predominant and the resistance in the hole is negligible.

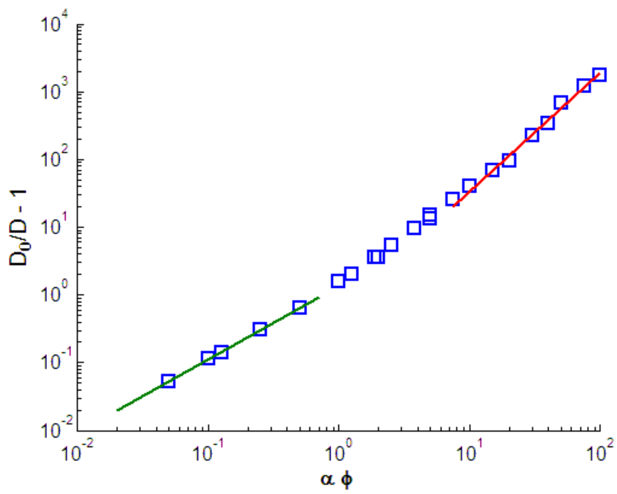

Figure 3, Resistance to the diffusion (D_0/D-1) as function of the factor a f, for the case of circular configuration (σ=10)

Random systems

For random system due to the higher computational cost, only the circular shape of platelets has been investigated; this is indeed the one which has to be considered to mimic as best the clay platelets in the nanocomposite structures. Figure 4 shows the permeability decay in randomly distributed structures in comparison with the one in ordered geometries at different slit shapes; as one can see, there is a large gap between barrier effect observed in ordered structures and the one guaranteed by structures where the platelets are randomly distributed.

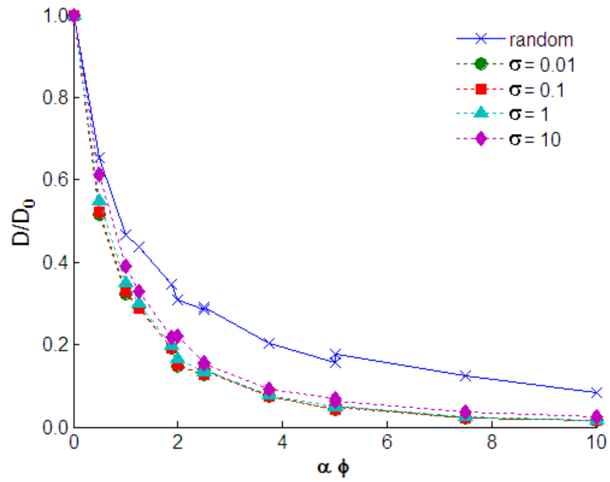

Figure 4, Comparison between the permeability ratio in ordered systems at different values of slit shape and in the randomly distributed systems

Indeed, the random distribution of the platelets is not able to guarantee a remarkable barrier effect because of the formation of clusters of lamella and shortcuts that the penetrant can use to diffuse faster. In this concern, therefore, the simulations have shown that this effect is more pronounced in a three-dimensional system than in 2-D [16]: in fact, contrary to what happens in 2-D systems, even at high values of slit shape (such as of the same order of magnitude of the size of the flake), random structures cannot be modeled by using a ordered approach because there exist in anyway a remarkable difference between the permeability decay in the two cases.

The results in case of random systems are then represented in Figure 5 in comparison with all the models previously mentioned.

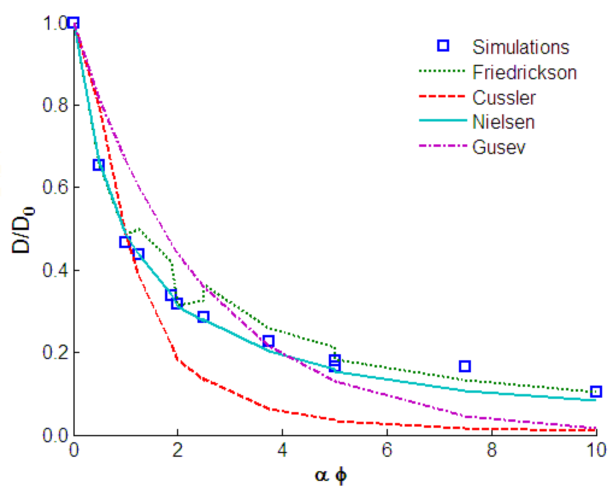

Figure 5, Permeability ratio in randomly distributed system in comparison with the models

As one can see, simulation results show a good agreement with the Friedrickson and an even better match with the prediction of the Nielsen equation; on the other hand the model due to Cussler cannot approach the trend of the simulation even changing the fitting parameter μ and also the equation due to Gusev, substantially exponential refers to a behavior that is not followed to the simulation results obtained in the present work. It has to be considered, indeed, that Cussler developed his approach in the approximation of 2-D structures and the formula subsequently proposed was just an extension for the tri-dimensional case; Gusev on the other side gave was mainly focused on the simulation approach to the problem and the formula he proposed was a sort of fitting equation for his results whose parameter had substantially no physical meaning.

Surprisingly, the model that seems to work better in defining the decrease in permeability due to filler addition is the one due to Nielsen, which in its simplicity is able to catch the essential feature of the problem and results thus able to mimic the resistance to the permeation in nanocomposite material as obtained by the present numerical results.

Conclusions

In this work the barrier properties of a nanocomposite film were modeled and the diffusion of small molecules in a composite media has been simulated from a macroscopic point of view, using a finite volume method. Simulations were carried out on three-dimensional geometries, in which an impermeable phase, consisting in platelets in different configurations, was placed in the simulation box.

At first the effect of the shape of the lamellae have been discussed considering ordered structures; not negligible effects were observed since the barrier properties significantly decreased passing from a tape shape to square or circular platelets. Considering the behavior of the barrier effect in these structure, furthermore, two different trends were observed, the first one linear with the factor $\alpha\ \phi$, and the second one quadratic, related respectively to the hole resistance and to the wiggling of gas molecules around the flakes.

More realistic structures were also developed by placing circular platelets randomly in the simulation box. The behavior of the barrier effect in these structure has been analyzed and compared with the previous one and to the model already describe in the technical literature.

The results showed that the ordered structures hypothesis is too restrictive in modeling diffusion in nanocomposite systems and it overestimates dramatically the barrier effect achieved by the presence of the inorganic filler. On the other hand, Nielsen model, despite its simplicity, proved to be able to represent very accurately the present simulation results and seems to have also high potentialities in the prediction of real materials behavior.

Acknowledgement

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