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Homogenization of moisture diffusing behaviour of composite materials with impermeable or permeable fibres – Application to porous composite materials

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Abstract

In order to predict the long-term durability of polymer matrix composite materials submitted to humid environments, the moisture diffusion behaviour has to be investigated. The knowledge of the effective diffusivity is actually required, for estimating the moisture content of polymer based fibre reinforced materials, even when a basic behaviour such as Fick's law is assumed to occur. **The original contribution of the present work is to provide new analytical solutions for the effective diffusivities from the solving of unit cell problems on representative volume elements by means of several multi-scale approaches.** Composite materials with impermeable or permeable fibres are extensively investigated. The proposed approaches are extended to the practical case of composite materials containing realistic voids volume fractions.

Keywords: homogenization, effective moisture diffusivity, closed-form solutions.

1. Introduction

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Composite materials absorb moisture during their service life, principally through the resin, but also through the fibres when they are permeable [1]. In numerous cases, the moisture kinetic follows the classical Fick's law, according to [2, 3]. The knowledge of the moisture diffusivity and the appropriate boundary conditions enables calculating the time-dependent moisture content field in the composite material which can be useful for determining the corresponding mechanical states, for instance. The purpose of this paper is to **propose original analytical solutions for** the effective moisture diffusivity of polymeric composite materials with impermeable or permeable fibres, through several appropriate scale-transition models. The effective diffusivity is deduced from solving a unit cell problem on a Representative Volume Element (RVE). The defined RVE is submitted to a macroscopic moisture gradient inducing local fields and gradients within the RVE. The effective diffusivity is calculated by considering the discontinuity of the moisture contents and the continuity of the moisture flux that occur at the boundary between the composite plies constituents (i.e. the polymer matrix, on the one hand, and the reinforcing fibre, on the other hand). At the interface between two materials exhibiting heterogeneous moisture diffusion behaviour, only the continuity of the chemical potentials is actually assumed to be satisfied [4]. Thus, a parameter representative of the gap in terms of moisture content experienced by two adjacent constituents is introduced in the unit cell problem to be solved **and therefore appears in the proposed expressions for the effective diffusivities**. In the case of permeable fibres, inverse approaches enable the determination of the moisture diffusivity of the fibres. A comparison with effective diffusivities calculated according to finite elements methods is also achieved. Finally, the presented multi-scale approaches are extended to porous composite materials so that the influence of void contents on the effective diffusivity would also be discussed.

2. Effective moisture diffusivity

The multi-scale approaches, considered in the present work, are based on the solving of unit cell problems on various Representative Volume Element (RVE). Several approaches are used in order to estimate the effective moisture diffusivity of fibre-reinforced polymer matrix composite plies: a three phases model, a self-consistent model and a finite elements approach. Each of them is extensively described in the following paragraphs.

2.1 Three phases model

The RVE (Figure 1) is composed of the reinforcing fibre, the polymer matrix and the equivalent homogeneous medium, the properties of which have to be determined. The fibre radius and volume will be denoted by r_f and V_f, respectively, whereas the corresponding quantities, for the matrix, will be denoted by r_m and V_m. In this configuration, the application of a moisture content flux $\vec{G}$ on the RVE enables to obtain the equivalent diffusing behaviour**.**

The unit cell problem is defined by the following system of equations:

$$\begin{cases} \mathrm{div}\vec{q} = 0 \\ \vec{q} = -D\,\overrightarrow{\mathrm{grad}}\,C \\ \left\| \vec{q}.\vec{n} \right\| = 0 \ \text{ at the interface fibre/matrix} \\ \left\| C \right\| \neq 0 \ \text{ at the interface fibre/matrix} \end{cases} \tag{1}$$

where $\vec{q}$ is the moisture content flux, $\vec{n}$ the normal vector and D the diffusion coefficient.

The sign $\| \|$ stands for the moisture contents and flux at the interfaces. For cylindrical constituents, $\mathrm{div}\vec{q} = \mathrm{div}\left(-D\,\overrightarrow{\mathrm{grad}}\,C\right) = -D\left(\frac{1}{r}\frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2 C}{\partial \theta^2}\right)$ **and** the moisture content field solution of the unit cell problem (1) reads (r and θ standing for the radial and circumferential coordinates respectively):

$$\begin{cases} C(r,\theta) = A_f\, r\cos(\theta) & \text{in the fibre} \\ C(r,\theta) = (A_m r + \frac{B_m}{r})\cos(\theta) & \text{in the matrix} \\ C(r,\theta) = G\, r\cos(\theta) & \text{in the equivalent medium} \end{cases} \tag{2}$$

where A_f, A_m, B_m and G are unknown constants.

Let us consider, i) the boundary conditions, ii) the continuity and discontinuity conditions at the interfaces and iii) the permeability of the fibres.

<u>At r=r_m</u>

The continuity of the moisture contents at the boundary between the equivalent medium and the matrix is considered:

$$A_m r_m^2 + B_m - G r_m^2 = 0 \tag{3}$$

The moisture content flux in the matrix is equal to the moisture content flux in the equivalent medium, so that $D_m \left.\frac{\partial C}{\partial r}\right|_{r_m} = D_{eff} \left.\frac{\partial C}{\partial r}\right|_{r_m}$, thus:

$$D_m A_m r_m^2 - D_m B_m - D_{eff}\, G r_m^2 = 0 \tag{4}$$

where D_m and D_{eff} are the diffusion coefficients of the matrix and the equivalent medium, respectively.

At r=r_f

The continuity of the flux between fibre and matrix, (which writes $D_f \left.\frac{\partial C}{\partial r}\right|_{r_f} = D_m \left.\frac{\partial C}{\partial r}\right|_{r_f}$), is considered:

$$D_m A_m r_f^2 - D_m B_m - D_f A_f r_f^2 = 0 \tag{5}$$

where D_f is the diffusion coefficient of the fibre.

The discontinuity of the moisture contents between fibre and matrix involves a moisture content gap: $C_f = \alpha C_m$, so that the following relation has to be satisfied:

$$\alpha A_m r_f^2 + \alpha B_m - A_f r_f^2 = 0 \tag{6}$$

where α is a constant representative to the moisture content gap between fibre and matrix (α can be defined if and only if $C_m \neq 0$ i.e. for a composite having a permeable matrix).

The equations (3), (4), (5) and (6) constitute a system of four equations with four unknown constants (A_m, B_m, A_f, G):

$$\begin{bmatrix} r_m^2 & 1 & -r_m^2 & 0 \\ D_m r_f^2 & -D_m & 0 & -D_f r_f^2 \\ D_m r_m^2 & -D_m & -D_{eff} r_m^2 & 0 \\ \alpha r_f^2 & \alpha & 0 & -r_f^2 \end{bmatrix} \begin{bmatrix} A_m \\ B_m \\ G \\ A_f \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \tag{7}$$

In order to obtain a set of non-trivial solutions for the unknown constants, the mathematical condition is that the determinant of the matrix presented in the left-hand side of (7) must be equal to zero. Thus, making this determinant equal to zero, the effective diffusion coefficient is obtained:

$$D_{eff} = D_m \frac{D_m(1-\frac{r_f^2}{r_m^2}) + \alpha D_f(1+\frac{r_f^2}{r_m^2})}{D_m(1+\frac{r_f^2}{r_m^2}) + \alpha D_f(1-\frac{r_f^2}{r_m^2})} \tag{8}$$

For a cylindrical geometry of the RVE, the ratio $\frac{r_f^2}{r_m^2}$ corresponds to the fibre volume fraction v_f. As aconsequence, the expression (8) can be expressed as follows:

$$\frac{D_{eff}}{D_m} = \frac{(1-v_f) + \alpha \frac{D_f}{D_m}(1+v_f)}{(1+v_f) + \alpha \frac{D_f}{D_m}(1-v_f)} \tag{9}$$

Starting from the knowledge of D_{eff} and D_m, equation (9) enables the determination of D_f.

By introducing the parameter $\psi = \alpha \frac{D_f}{D_m}$, expression (9) becomes:

$$\frac{D_{eff}}{D_m} = \frac{(1-v_f) + \psi(1+v_f)}{(1+v_f) + \psi(1-v_f)} \tag{10}$$

In the particular case, when $\psi = 0$, we get the classical Hashin's expression [5] for composite materials with impermeable fibres:

$$\frac{D_{eff}^{impr}}{D_m} = \frac{1-v_f}{1+v_f} \tag{11}$$

Figure 2 shows the evolution of the effective diffusion coefficient, obtained through equation (10), as a function of the parameter ψ, for different fibre volume fractions. **In this representation, the parameter ψ can be assimilated to a fibre permeability index. A fibre permeability index lower than one involves that the fibres reduce the velocity of the**

diffusion process in the composite material (case the most frequently encountered in practice), by comparison to the reference diffusive behaviour of the neat resin. For a material constituted by a quasi impermeable matrix, on the one hand, and by fibres presenting a strong permeability, on the other hand, ψ should be higher than 1. As a consequence, this representation, featuring the parameter ψ, enables to consider numerous diffusive behaviours.

The diffusion coefficient is a growing function of the parameter ψ. It nevertheless tends towards a constant level for a value of ψ depending on the fibre volume fraction v_f. The intersection of the displayed curves, observed at $\psi = 1$, actually corresponds to $D_{eff} = D_m$. The regions with $\psi < 1$ and $D_{eff} < D_m$ characterize composite materials whose fibres present a weak permeability. The fact that the curves with stronger reinforcements volume fractions are below those with weaker fibres volume fractions reveals the attenuation effect due to the fibres on the moisture diffusion process.

2.2 Self-consistent model

In this model, the fibre, that fills a volume V_f, is embedded in an infinite matrix, that takes up a volume V_{eq}, and has the researched equivalent diffusive properties (Figure 3).

In this configuration, the application of a moisture content flux $\vec{G}$ on the RVE enables to obtain the equivalent diffusing behaviour.

The moisture content field solution of the unit cell problem **(satisfying** $\mathrm{div}\vec{q} = 0$**)** is:

$$\begin{cases} C(r,\theta) = A_f \; r\cos(\theta) & \text{in } V_f \\ C(r,\theta) = \left(G\,r + \dfrac{B_{ac}}{r} \right)\cos(\theta) & \text{in } V_{eq} \end{cases} \tag{12}$$

where A_f, B_{ac} and G are unknown constants.

The homogeneous equivalent behaviour is defined as follows:

$$D_{eff} < \overrightarrow{grad}\ C(y) > = v_f D_f < \overrightarrow{grad}\ C(y) >_{V_f} + v_m D_m < \overrightarrow{grad}\ C(y) >_{V_m} \qquad (13)$$

where the quantity $\langle \overrightarrow{grad} C(y) \rangle_V$ denotes the average of the quantity $\overrightarrow{grad} C(y)$ over the volume V as follows:

$$\langle \overrightarrow{grad} C(y) \rangle_V = \frac{1}{|V|} \int_{\partial V} C \vec{n} ds$$

∂V is the outer surface delimiting V, whereas $\vec{n}$ is the unit vector normal to this border.

Finally, equation (13) and the interface conditions lead to the following system of equations:

$$\begin{bmatrix} r_f^2 & 1 & -r_f^2 \\ D_{eff}\, r_f^2 & -D_{eff} & -D_f\, r_f^2 \\ D_{eff} - D_m & 0 & v_f\,(D_m - D_f) \end{bmatrix} \begin{bmatrix} G \\ B_{ac} \\ A_f \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \qquad (14)$$

Equating the determinant of expression (14) to zero, one obtains the following equation of the second degree in D_{eff}:

$$D_{eff}^2 + D_{eff}\,[D_m(2v_f - 1) + D_f\,(1 - 2v_f)] - D_f D_m = 0 \qquad (15)$$

It is easy to check that, the single positive root of (15) satisfies:

$$\frac{D_{eff}}{D_m} = \frac{1}{2}\left(\frac{D_f}{D_m}(2v_f - 1) + (1 - 2v_f) + \sqrt{\frac{4D_f}{D_m} + \left[\frac{D_f}{D_m}(1 - 2v_f) + (2v_f - 1) \right]^2} \right) \quad (16)$$

For an impermeable fibre (i.e, introducing the condition $D_f = 0$) the normalised effective diffusivity simplifies as follows:

$$\frac{D_{eff}}{D_m} = 1 - 2v_f \quad (17)$$

The domain of validity of expression (17) is limited to v_f values lower than 0.5. In order to improve the results of this model and to extend its domain of validity to stronger fibre volume fractions, the self-consistent model was associated to an iterative calculation procedure (IP), following the approach detailed in references [6, 7]. The final fiber volume fraction is reached by introducing step by step a partial volume fraction f_p ($f_p = \frac{v_f}{n}$ **where n is the number of iterations**).

Figure 4 reports the results obtained with the self-consistent model associated, or not, to the iterative calculation process, which are compared to the three phases approach. The results of the self-consistent model become closer to those provided by the three phases model, particularly for weak fibre volume fraction, when the iterative calculation procedure is followed.

2.3 Comparison with numerical approaches

Numerical methods based on a resolution of the cellular problem by finite elements [8] or by finite differences can be used in order to characterize the diffusive behaviour of composites materials. The considered unit cells are bidimensional and symmetrical. The resolution of the

cellular problem provides the moisture content field in the unit cell and the effective diffusion coefficient is determined from the relation:

$$D_{eff} \left\langle \overrightarrow{grad}\ C(y) \right\rangle = D_{eff}\, \vec{G} = v_f\ D_f \left\langle \overrightarrow{grad}\ C(y) \right\rangle_{V_f} + (1 - v_f)\, D_m \left\langle \overrightarrow{grad}\ C(y) \right\rangle_{V_m} \qquad (18)$$

where $\left\langle \overrightarrow{grad}\ C(y) \right\rangle_{V_m}$ and $\left\langle \overrightarrow{grad}\ C(y) \right\rangle_{V_f}$ are the average concentration gradients over the volume of the matrix and that of the fibre, respectively.

2.3.1 Case of impermeable fibres

Let us first consider a unidirectional composite with impermeable fibres. Such a composite exhibits a transversaly isotropic behaviour with regard to moisture diffusion. In order to evaluate the effective diffusivity of the unit cell, it is sufficient to solve a stationary one-dimensional diffusion problem featuring Dirichlet-type boundary conditions on the two opposite edges (corresponding to a uni-axial concentration gradient G). The flux in the other directions is considered to be null. Since the fibre is impermeable, the flux will fall to zero in its vicinity [9]:

$$\frac{\partial C}{\partial n} = 0 \qquad (19)$$

$\vec{n}$ is the normal vector to the surface of the fibre (Figure 5).

The cellular problem, corresponding to square or hexagonal arrangements of the fibres (Figure 5), was achieved through the finite element method by using Matlab software. Figure 6 shows the resulting reduced effective diffusivity as a function of the fibre volume fraction for hexagonal and square arrangements and those obtained according to the three phases model (11). No difference occurs for the reduced diffusivity, whatever the considered fibre arrangement, for reinforcements volume fractions included in the range 0 - 40 %. Moreover,

in this range of fibre volume fractions, the numerical approaches are close to the results obtained through the three phases model. For reinforcements volume fractions above 40 %, the results provided by the numerical approach significantly depends on the considered geometrical arrangement for the unit cell. The discrepancy between the estimated effective diffusivities increases as a function of the fibre volume fraction. Only the numerical predictions obtained by assuming a hexagonal array of fibres remain close to those provided by the three phases model (up to a fibre volume fraction of 0.8). The numerical value for diffusivity is zero for a fibre volume fraction equal to 0.785 ($\pi/4$), which represents the upper limit value of reinforcement for a square array, whereas for a hexagonal arrangement, this value is close to 0.9 ($\frac{\pi}{2\sqrt{3}}$). Only, the analytical approach enables to calculate the reduced effective diffusivity for $v_f = 1$ (this should nevertheless be considered as a purely theoretical situation, without practical applications).

2.3.2 Case of permeable fibres

In the case of a unidirectional composite with permeable fibres, diffusion happens through two media: the matrix and the fibres, the diffusivities of which are strongly heterogeneous. As stated earlier at the time of the analytical solving of the cellular problem, there still exists a concentration gap at the interface fibre/matrix.

In order to find a numerical solution to this problem, spatial and temporal finite difference discretization is required. The numerical scheme used here is explicit.

Figure 7 shows the reduced effective diffusivity obtained by the actual numerical approach and the analytical expression (10). The obtained values are very similar, particularly for weak fibre volume fractions.

3. Effective moisture diffusivity of porous composite materials

The presence of voids in composite materials, is known to induce significant decrease of the mechanical properties, even at very weak volume fraction [10,11]. **Moreover, in humid environment they also affect the moisture absorption [12,13].** The aim of this part is to investigate the effect of voids on the moisture diffusion process in composite materials.

3.1 Composite materials with porous matrix

We assume a perfect adhesion between fibres and matrix and that the voids are only embedded in the matrix. Therefore, the first step is to determine the effective diffusion coefficient of the porous matrix.

A moisture content gap, denoted by parameter α_{mv}, is introduced at the interface between matrix and voids. The volume fractions of voids are often weak (i.e. lower than 5 %) in composite materials, so that the diluted distribution approach, illustrated by the RVE presented in Figure 8, can be used. In this approach, the application of a moisture content flux $\vec{G}$ on the RVE enables to obtain the equivalent diffusing behaviour.

The moisture content field solution of the unit cell problem is:

$$\begin{cases} C(r\theta) = A_v \; r\cos(\theta) & \text{in the fibre} \\ C(r\theta) = (Gr + \dfrac{B_m}{r})\cos(\theta) & \text{in the matrix} \end{cases} \tag{20}$$

where A_v, B_m and G are unknown constants.

The homogeneous equivalent behaviour is defined as follows:

$$D_{eff}^{m} \left\langle \overrightarrow{grad}\ C(y) \right\rangle = v_v\ D_v \left\langle \overrightarrow{grad}\ C(y) \right\rangle_{V_v} + v_m\ D_{eff}^{m} \left\langle \overrightarrow{grad}\ C(y) \right\rangle_{V_m} \tag{21}$$

where v_v is the volume fraction of voids whereas D_v denotes their diffusivity.

Finally, considering the interface conditions and the equation (21), the following system of equations is obtained:

$$\begin{bmatrix} D_m r_v^2 & -D_m & -D_v r_v^2 \\ D_{eff}^{m} - D_m & 0 & v_v (D_m - D_v) \\ \alpha_{mv} r_v^2 & \alpha_{mv} & -r_v^2 \end{bmatrix} \begin{bmatrix} G \\ B_m \\ A_v \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \tag{22}$$

By making the determinant of (22) equal to zero, the expression of the matrix effective diffusivity is obtained:

$$\frac{D_{eff}^{m}}{D_m} = 1 + 2\alpha_{mv} v_v \frac{\dfrac{D_v}{D_m} - 1}{\dfrac{D_v}{D_m} + 1} \tag{23}$$

The moisture content gap parameter can be defined by the ratio:

$$\alpha_{mv} = \frac{\rho_w}{M_m \rho_m (1 - v_v)} \tag{24}$$

where ρ_w and ρ_m are respectively the densities of water and matrix whereas M_m is the moisture content at saturation in the matrix.

The moisture content at saturation M_m, for a 5208 epoxy resin subjected to a relative humidity of 100 %, is 5.9 % according to Loos and Springer [14]. α_{mv} value is deduced from equation (24). For values of void volume fractions varying from 1 % to 5 %, there is no significant evolution of α_{mv}. As a consequence, an average value α_{mv} = 15 will be assumed for the gap parameter in the considered range of voids volume fractions.

Figure 9 shows the matrix effective diffusivity as a function of the normalized voids diffusivity D_v/D_m for different void volume fractions. We assume that the void diffusivity is higher than that of the matrix. The curves have the same departure point corresponding to $D_v = D_m = D_{eff}^m$. The effective diffusivity is a growing function of D_v/D_m while this very ratio remains weaker than around 10. Beyond this point, D_{eff}^m becomes nearly constant.

In order to estimate the effective diffusivity of a composite containing impermeable fibres, the matrix effective diffusivity is introduced in expression (11):

$$\frac{D_{eff}}{D_m} = [1 + 2\alpha_{mv} v_v \frac{\frac{D_v}{D_m} - 1}{\frac{D_v}{D_m} + 1}] \frac{1 - v_f}{1 + v_f} \tag{25}$$

Figure 10 shows the effective diffusivity as a function of the fibre volume fraction for a porous composite material exhibiting 0 %, 2 %, 5 % and 10 % void volume fractions, respectively. The fibres do not contribute to the diffusion process. Thus, an increase of the fibre volume fraction involves a decrease of the effective diffusivity.

3.2 Four phases approach: fibre, void, matrix, equivalent homogeneous medium

In this approach the void is modeled as a thin layer located between the fibre and the matrix (Figure 11).

In this case, the cellular diffusion problem through each layer is expressed as follows:

$$\begin{cases} \mathrm{div}\vec{q}(y) = 0 & \text{in each phase } V_\alpha \\ \vec{q} = -D\,\overrightarrow{\mathrm{grad}}\,C & \text{in each phase } V_\alpha \\ \left\| \vec{q}.\vec{n} \right\| = 0 & \text{at interfaces} \\ \left\| C \right\| \neq 0 & \text{at interfaces} \end{cases} \tag{26}$$

The solution fields respect the forms:

$$\begin{cases} C(r,\theta) = A_f\, r\cos(\theta) & \text{in the fibre} \\ C(r,\theta) = (A_v r + \dfrac{B_v}{r})\cos(\theta) & \text{in the voids} \\ C(r,\theta) = (A_m r + \dfrac{B_m}{r})\cos(\theta) & \text{in the matrix} \\ C(r,\theta) = Gr\cos(\theta) & \text{in the equivalent medium} \end{cases} \tag{27}$$

where A_f, A_v, A_m, B_v, B_m and G are unknown constants.

The conditions of flux continuities and moisture content discontinuities assumed to hold at each interfaces involve the following set of equations:

$$\begin{bmatrix} 0 & 0 & \alpha_{fv}\, r_f^2 & \alpha_{fv} & -r_f^2 & 0 \\ 0 & 0 & D_v\, r_f^2 & -D_v & -D_f\, r_f^2 & 0 \\ \alpha_{mv}\, r_v^2 & \alpha_{mv} & -r_v^2 & -1 & 0 & 0 \\ D_m\, r_v^2 & -D_m & -D_v\, r_v^2 & D_v & 0 & 0 \\ r_m^2 & 1 & 0 & 0 & 0 & -r_m^2 \\ D_m\, r_m^2 & -D_m & 0 & 0 & 0 & -D_{eff}\, r_m^2 \end{bmatrix} \begin{bmatrix} A_m \\ B_m \\ A_v \\ B_v \\ A_f \\ G \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \tag{28}$$

where α_{fv} and α_{mv} are moisture content gaps corresponding to the interfaces voids/fibre and voids/matrix respectively. The knowledge of moisture content at saturation and diffusivities of composite and matrix leads to the determination of gap parameters and enables estimating the fibre diffusivity. By making the determinant of (28) equal to zero, one actually obtains the following expression of the normalized effective diffusivity:

$$\frac{D_{eff}}{D_m} = \frac{(1-kv_f)[1+k+\alpha_{fv}\frac{D_f}{D_v}(k-1)]+\alpha_{mv}(1+kv_f)[\frac{D_v}{D_m}(k-1)+\alpha_{fv}\frac{D_f}{D_m}(1+k)]}{(1+kv_f)[1+k+\alpha_{fv}\frac{D_f}{D_v}(k-1)]+\alpha_{mv}(kv_f-1)[\frac{D_v}{D_m}(1-k)-\alpha_{fv}\frac{D_f}{D_m}(1+k)]} \tag{29}$$

where, $k = \frac{v_v + v_f}{v_f}$, v_v and v_f being the void and fibre volume fractions, respectively.

By introducing $\phi = \alpha_{mv}\frac{D_v}{D_m}$ and $\psi = \alpha_{fv}\frac{D_f}{D_m}$, equation (29) becomes:

$$\frac{D_{eff}}{D_m} = \frac{(1-kv_f)[1+k+\alpha_{mv}\frac{\psi}{\phi}(k-1)]+(1+kv_f)[\phi(k-1)+\alpha_{mv}\psi(1+k)]}{(1+kv_f)[1+k+\alpha_{mv}\frac{\psi}{\phi}(k-1)]+(1-kv_f)[\phi(k-1)+\alpha_{mv}\psi(1+k)]} \tag{30}$$

Assuming that moisture diffusion in void is faster than in any other constituents, the set of inequations $\alpha_{fv} \langle 1$ and $\alpha_{mv} \rangle 1$ is considered. According to the literature, α_{fv} = 0.2 (i.e. $\psi = 4.18$) would for instance correspond to an interface jute fibre/voids [15].

Figure 12 shows the evolution of the effective diffusivity of a composite material with permeable fibres in the case that $\psi = 4.18$ and $\phi = 150$ ($D_v/D_m = 10$ and $\alpha_{mv} = 15$) for various volume fractions of voids. A large increase of the diffusivity as a function of the rate of voids is obtained. For 2 % of voids and a fibre volume fraction equal to 70 %, an increase of about 35 % is observed. For 10 % of voids and the same fibre volume fraction, the increase in terms of diffusivity is about 100 %. These values reveal the strong sensitivity of the effective diffusivity to the void volume fraction.

Impermeable fibres

The expression of the effective diffusion coefficient for composites with impermeable fibres is obtained by considering $D_f = 0$ (i.e. $\psi = 0$) in expression (30), which simplifies as follows:

$$\frac{D_{eff}}{D_m} = \frac{(1-kv_f)(1+k)+\phi(1+kv_f)(k-1)}{(1+kv_f)(1+k)+\phi(1-kv_f)(k-1)} \tag{31}$$

By puting $v_v = 0$ (i.e. $k = 1$) in (31), we recognize the expression (11) of the normalized effective diffusivity.

Figure 13 shows the effective diffusivity as a function of the fibre volume fraction for a composite material containing respectively 0 %, 2 %, 5 % and 10 % in volume of voids. We note that the difference between the diffusion coefficients is proportional to the voids volume fraction. The difference observed between the effective diffusivities for non-porous and porous materials is more important than in the case of permeable fibres: for the volume fractions of fibres and voids respectively equal to 10 % and 70 %, the effective diffusion coefficient is 26 times more important than that of void free composite.

A decrease in the effective diffusion coefficient as a function of v_f, in the case of a non porous material, is observed. The presence of voids in the case that impermeable fibres are considered does not only tend to reduce the damping effect of the fibres on the effective diffusivity but also undertakes the influence of the matrix on the diffusive behaviour of the composite. Such a behaviour does not occur anymore when the effective diffusivity of the composite material is calculated by using the effective diffusivity of porous matrix deduced from the diluted approach (Figure 10).

3.3 Void modelling with self-consistent model

The basic idea of void modelling by the self-consistent model is to consider the composite RVE as consisting of three heterogeneous phases: fibre, void (represented by a thin layer surrounding the fibre) and the equivalent media (Figure 14).

In this case, the solution fields satisfy:

$$\begin{cases} C(r,\theta) = A_f\, r\cos(\theta) & \text{in the fibre} \\ C(r,\theta) = (A_v r + \dfrac{B_v}{r})\cos(\theta) & \text{in the void} \\ C(r,\theta) = (Gr + \dfrac{B_{ac}}{r})\cos(\theta) & \text{in the equivalent meduim} \end{cases} \tag{32}$$

where A_f, A_v, B_v, B_{ac} and G are unknown constants.

Although the void and the equivalent medium are of different nature, moisture continuity is imposed between them since they are not at the same scale. In this case, the homogeneous equivalent behaviour is defined as follows:

$$D_{eff}\left\langle \overrightarrow{grad}\,C(y)\right\rangle = v_f D_f \left\langle \overrightarrow{grad}\,C(y)\right\rangle_{V_f} + v_m D_{eff}\left\langle \overrightarrow{grad}\,C(y)\right\rangle_{V_m} + v_v D_v \left\langle \overrightarrow{grad}\,C(y)\right\rangle_{V_v} \tag{33}$$

The conditions of flux continuities and moisture content continuity and discontinuities at the interfaces with the homogeneous equivalent behaviour, lead to the following set of equations:

$$\begin{bmatrix} r_f^2 & -\alpha_{fv} r_f^2 & -\alpha_{fv} & 0 & 0 \\ D_f r_f^2 & -D_v r_f^2 & D_v & 0 & 0 \\ 0 & r_v^2 & 1 & -r_v^2 & -1 \\ 0 & D_v r_v^2 & -D_v & -D_{eff}\, r_v^2 & D_{eff} \\ v_f\,(D_m - D_f) & v(D_m - D_v) & 0 & (D_{eff} - D_m) & 0 \end{bmatrix} \begin{bmatrix} A_f \\ A_v \\ B_v \\ G \\ B_{ac} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \tag{34}$$

Making the system determinant equal to zero provides the expression of the effective diffusivity. The expression of composite diffusivity for impermeable fibres is obtained by considering $D_f = 0$ and $\alpha_{fv}=0$ in the system determinant, then:

$$\frac{D_{eff}}{D_m} = \frac{1}{2(1+k)}\left[\frac{D_v}{D_m}(1+k(2v_v-1)) + (1+k(1-2v_v)) + \sqrt{4\frac{D_v}{D_m}(k^2-1) + \left[\frac{D_v}{D_m}(1+k(2v_v-1)) + 1 + k(1-2v_v)\right]^2}\right] \tag{35}$$

where $k = \dfrac{v_v + v_f}{v_f}$.

The fact that the expression of the diffusion coefficient of the composite is only a function of voids reveals a strong sensitivity to voids and implies that the composite diffusion behaviour is completely governed by the voids.

Figure 15 shows the effective diffusivity deduced from the self-consistent model approach for a composite material with 1 %, 5 % and 10 % void fractions for a *k* value corresponding to v_f = 0.7. The diffusivity for the void-free composite is calculated from expression (17) according

to an iterative process. The difference between the effective diffusivities for non-porous and porous materials becomes stronger as the void diffusivity increases. For 1 % of voids and D_v/D_m=10, the effective diffusion coefficient is 4.4 times more important than that of the void-free composite. This reveals a high sensitivity to void volume fraction.

Figure 16 illustrates the effects due to the void volume fraction on the predicted effective diffusivity calculated through the various approaches previously described in the present work. The approach based on the porous matrix is the less sensitive to the voids volume fraction, whereas the strongest effects due to the presence of voids is obtained with the four phases approach. The porous matrix and the four phases approaches have the same departing point corresponding to the diffusivity value of a free-void composite at v_f = 0.7 but the difference between both these approaches continuously increases with the void volume fraction.

4. Conclusion

New Closed-form solutions are proposed for calculating the effective diffusivities of fibre-reinforced composite plies as functions of the proper diffusivities of the constituents, their volume fraction and in the case that permeable fibres are considered, as a function of a representative parameter of the moisture content gap at the boundary between the constituents. These solutions also allow estimating the moisture diffusivity of a constituent, from the knowledge of the effective moisture diffusivity, through inverse approaches. A comparison with effective diffusivities calculated by using finite elements is also made and gives satisfactory results. A special attention is paid to the determination of the effective moisture diffusivity for composite materials containing voids, which are often met in practice

in such materials. The influence of void content on the diffusion process is emphasized through several numerical applications showing the strong interaction between porosity and the effective moisture transport behaviour of fiber-reinforced polymer matrix composite plies. In further works, the coupling between the moisture diffusivities and the mechanical stress states will be numerically investigated. **The correlation between the predicted and experimental results** will be checked.

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Figures

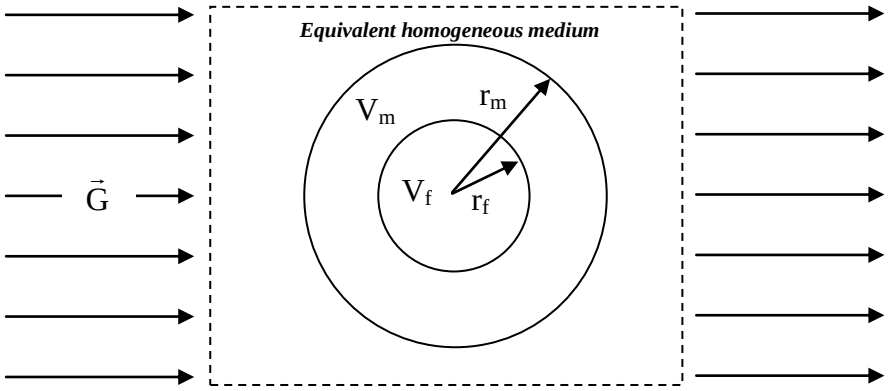

Fig. 1*: Representative Volume Element (RVE).*

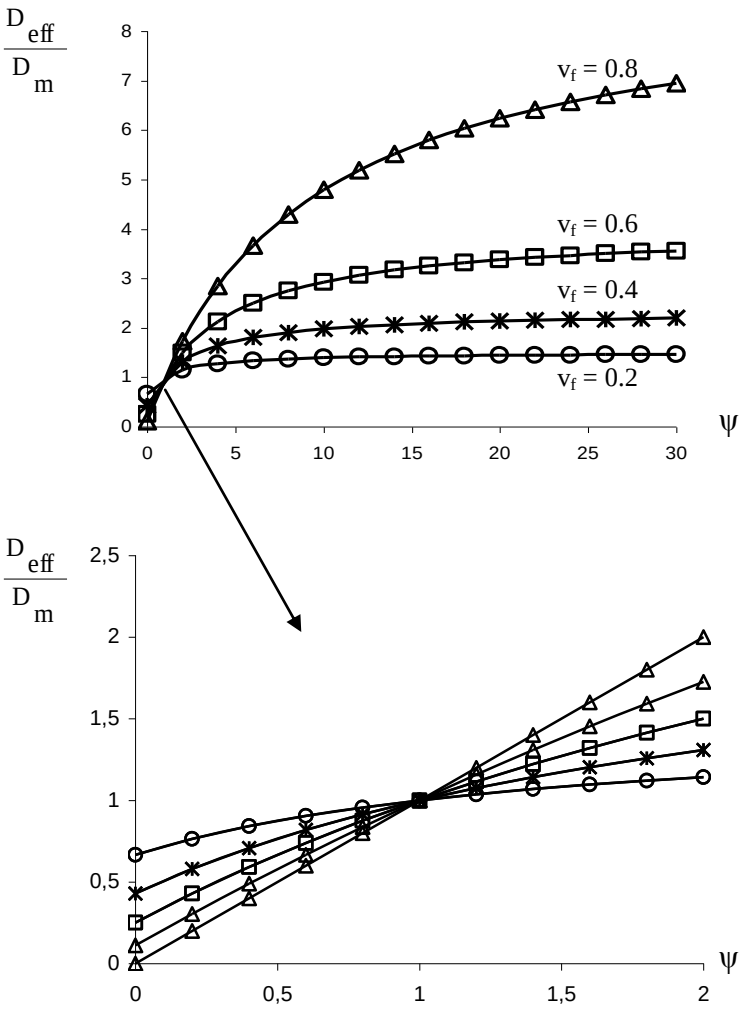

Fig. 2*: Dimensionless effective diffusivity as a function of ψ.*

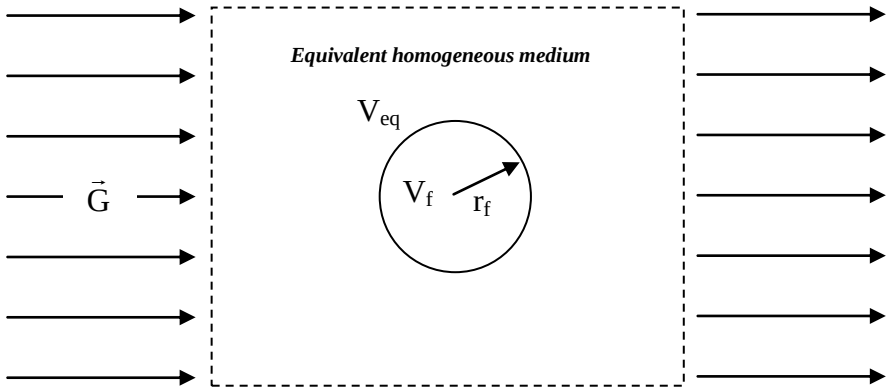

***Fig. 3**: Self-consistent model (RVE).*

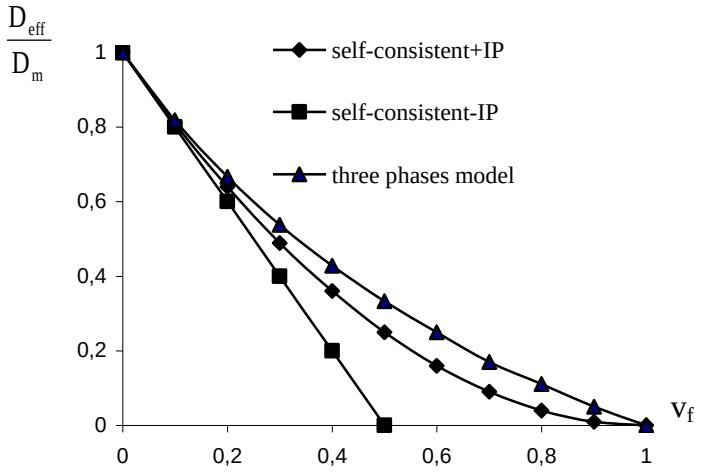

Fig. 4*: Effective diffusion coefficient deduced from the self-consistent model coupled and not coupled to iterative process (IP).*

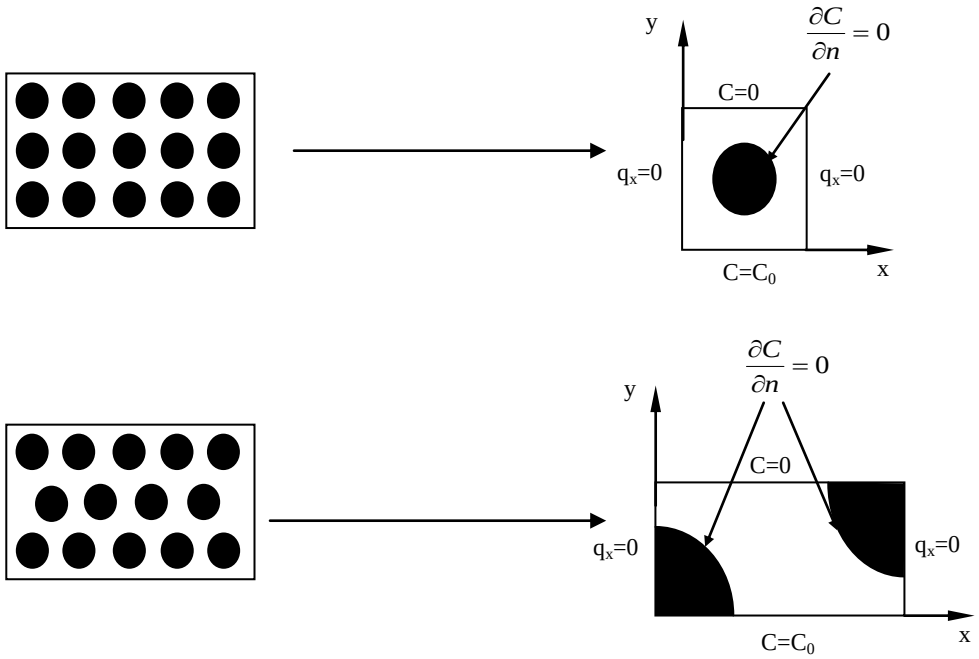

Fig. 5*: Square and hexagonal arrangement of the fibres.*

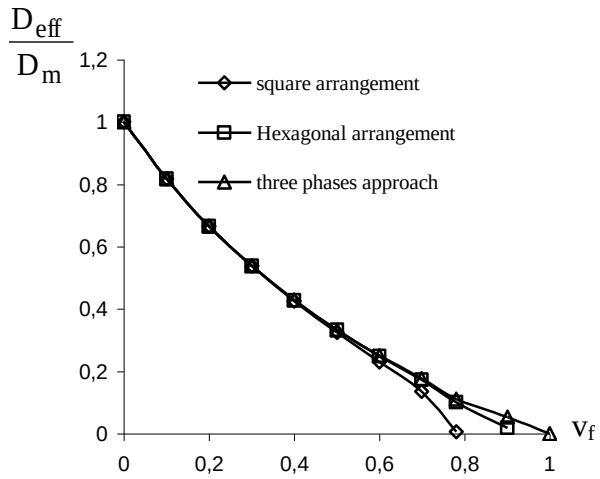

***Fig. 6**: Numerical approaches for composites with impermeable fibres.*

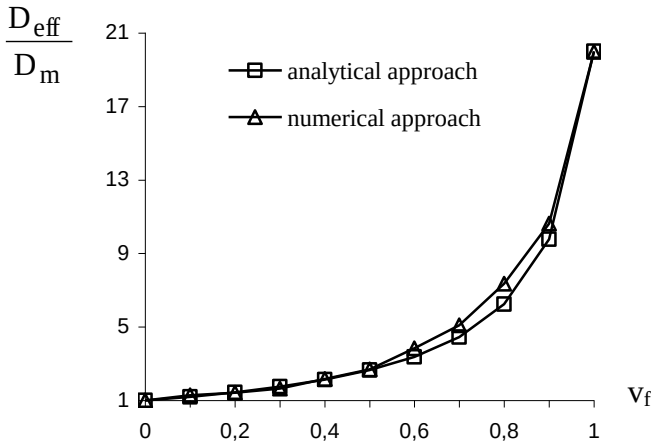

***Fig. 7**: Reduced effective diffusivity obtained from analytical and numerical approaches (ψ = 20).*

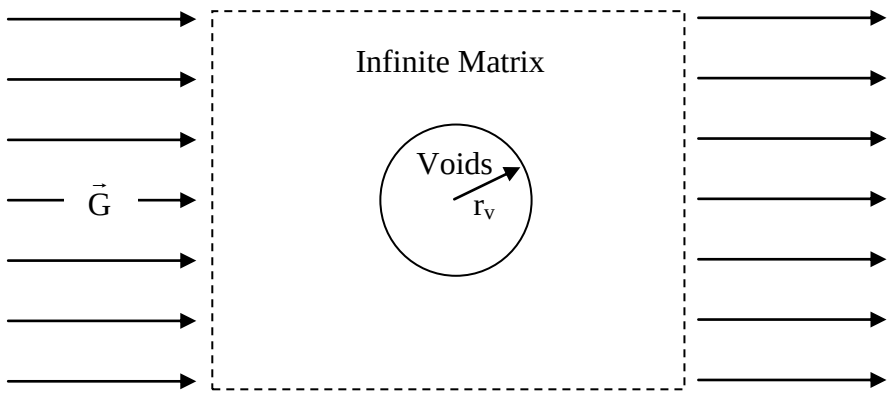

Fig. 8*: RVE of the porous matrix.*

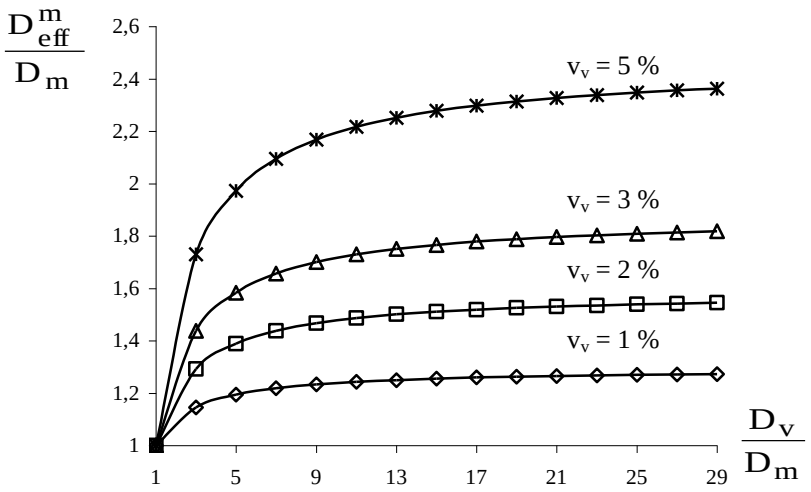

Fig. 9*: Dimensionless matrix effective diffusivity as a function of* D_v/D_m.

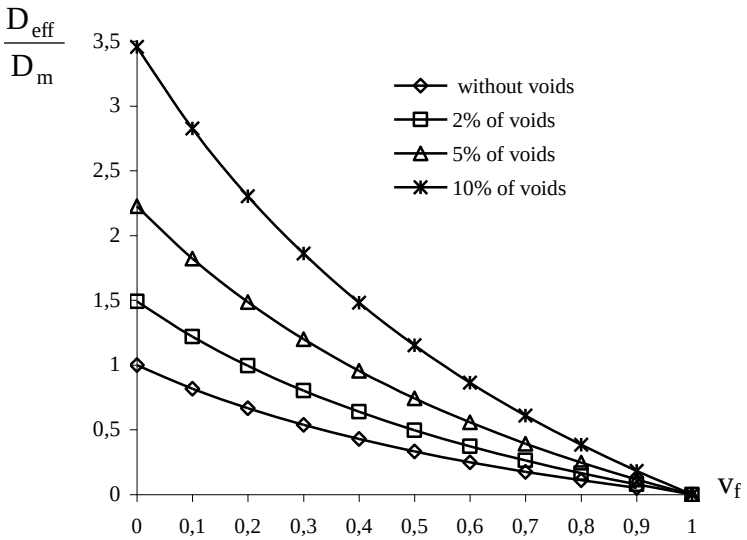

Fig. 10*: Void effects on the composite diffusivity in the case of impermeable fibres (D_v/D_m =10, α_{mv}=15).*

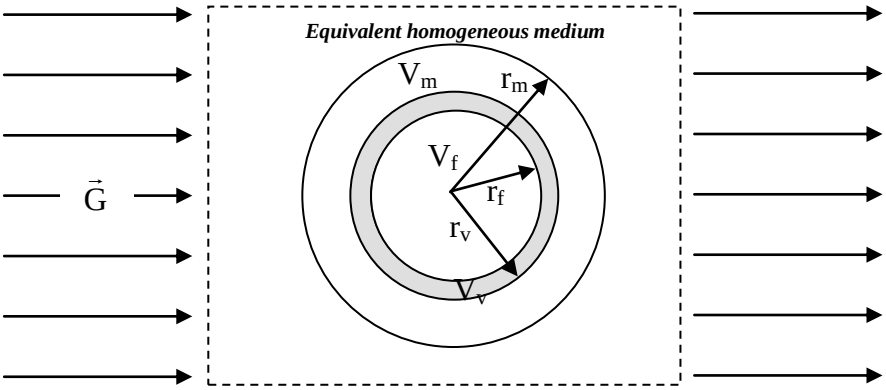

Fig. 11*: RVE of the four phases approach.*

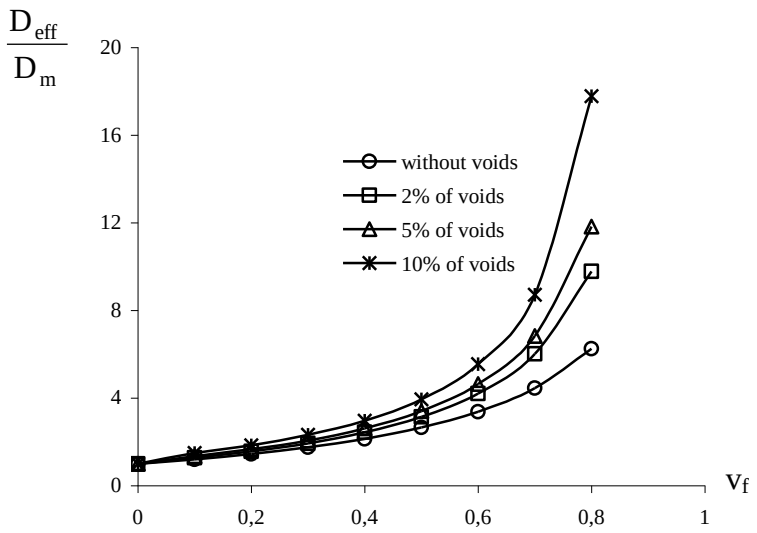

Fig. 12*: Void effects on the composite diffusivity in the case of permeable fibres (*ϕ*=150,* ξ*=4.18).*

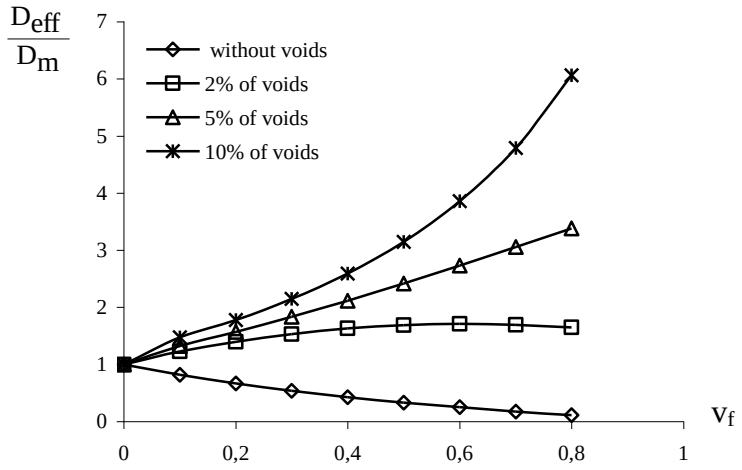

***Fig. 13**: Void effects on the composite diffusivity in the case of impermeable fibres (ϕ=150).*

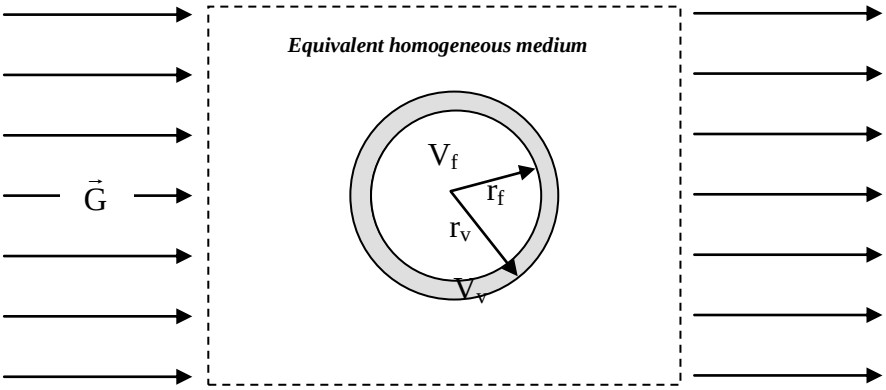

Fig. 14*: RVE of the the self-consistent model.*

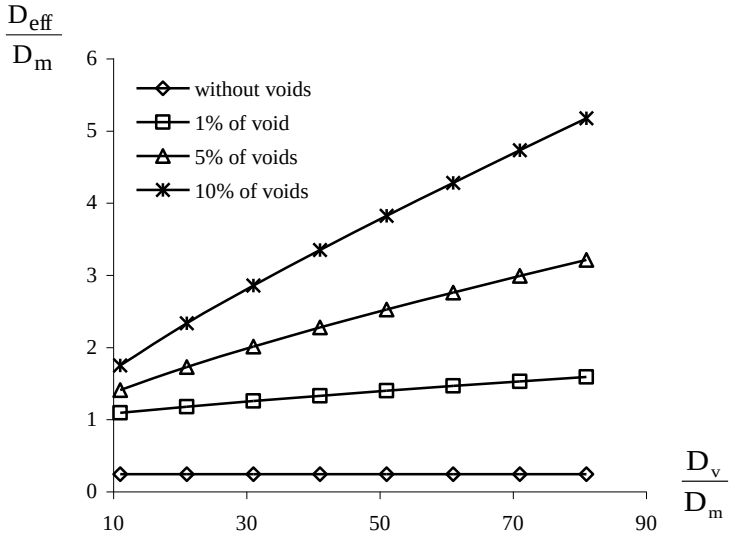

Fig. 15*: Void effects on the composite diffusivity in the case of impermeable fibres.*

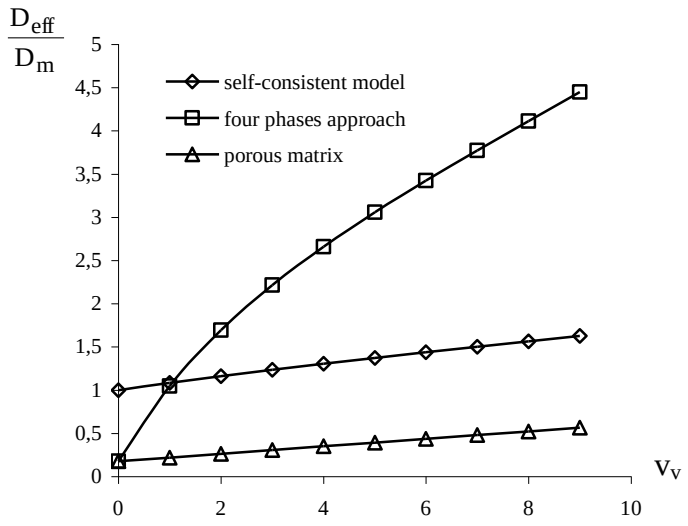

***Fig. 16**: Void content effects on the composite diffusivity in the case of impermeable fibres (D_v/D_m =10).*