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Modeling the effect of damage on diffusive behavior in a polymeric matrix composite material

Hocine Bourenane¹, Djelloul Gueribiz¹, Silvain Fréour²
and Frédéric Jacquemin²

In this work we investigate the effect induced by a cavity on the moisture diffusion behavior of a polymer matrix. Diffusion at the interface between the matrix and cavity is modeled owing to a thermodynamic approach. In this study, the effects related to crack shape and volume fraction on the overall diffusive behavior are accounted for. Two cases were treated: the case where the cavity is closed and located within the bulk of the matrix volume and another one where the cavity corresponds to an open crack. Two parameters were chosen for modeling the cavity: its geometric configuration and its volume fraction. In the case of a crack contained in the bulk of the material, several numerical examples have been performed for either a single cavity or for several cavities. In this second case, the effects related to the spatial dispersion of these cavities were investigated. The identification results for the diffusion coefficient show an increased sensitivity to the presence of damage in the form of cracks, especially when these cracks tend towards a flattened shape. In addition, a remarkable diffusion anisotropy takes place.

Keywords

Damage, polymer matrix, moisture diffusion, composites

Introduction

Polymer matrix composite materials have physico-chemical properties that make them predominant in many industrial sectors. Currently, their use is growing in many areas ranging from the leisure sector to that of nanotechnology. Although advanced technology is omnipresent in the manufacturing processes of these materials, their microscopic inspection often reveals numerous defects, including fiber/matrix debonding, fiber fracture. Moreover, matrix porosities or microcracks are also frequently detected.¹⁻⁴ These microstructural defects are considered as favorable sites for damage initiation and propagation as a consequence of mechanical or environmental loading. This damage can result in macro-defects such as inter-ply debonding or transverse cracking.^{5,6} The diffusive behavior modeling of damaged materials received less consideration compared to their mechanical behavior, for which the problem has received emphasis consideration in which more refined solutions have been proposed by several authors.⁷⁻⁹ In composites with polymeric matrix, the moisture uptake in the presence of damage in the

form of pores or microcracks is generally investigated taking into account the damage parameter. This parameter significantly affects the moisture uptake, as shown by the deviations reported to occur between the experimental moisture uptake collected on damaged specimen and those predicted by the classical theoretical models.¹⁰⁻¹⁶ However, particular attention has been paid to the study of a related problem in the work of Gueribiz et al.^{17,18} The authors modeled the effects induced by the presence of voids on the diffusion coefficient and the maximum moisture absorption capacity by assuming that at saturation these voids were filled

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with water in the liquid phase. These studies were realized assuming spherical shaped cavities only and were focused on the case of samples submitted to immersion conditions. In what follows, we thus propose a model of the moisture diffusion in the cavity based on a thermodynamic approach while remaining within the framework of an uncoupled approach (the diffusive behavior is supposed to be independent from the mechanical states in the considered material). First, we consider the case of a damaged matrix in which the damage is described as an elliptical-shaped internal cavity. Subsequently, complementary simulations will be carried out to study the effect of the cavity geometry and that of its volume fraction on the overall diffusive behavior. The case of an open crack will be treated in a separate section.

Diffusion in undamaged matrix

We consider the representative elementary volume (REV) of the undamaged matrix consisting of a continuous medium in which no porosity or other defect exists (Figure 1). On its boundaries is imposed the maximum capacity of moisture absorption (matrix moisture content $M_m(\%)$). In this work, it will be assumed that this quantity is related to the maximum moisture absorption capacity (matrix moisture content) $M_m(\%)$ according to the expression identified by Loos and Springer¹⁹ as valid over a wide range of polymers and polymer matrix composites²⁰

$$M_m = \alpha HR^\beta \quad (1)$$

where β and α depend on the polymer matrix.

Each point of the domain occupied by the REV is identified by its coordinates (x, y) . Under the assumption cited above, diffusion is supposed to be governed by Fick's law.²¹ In this case, the local problem to be solved in the REV can be expressed by

$$\begin{aligned} \frac{\partial m(x, y, t)}{\partial t} &= D \Delta m(x, y, t) \text{ in } \Psi \times R_*^+ \\ m(x, y, t) &= M_m(\%) \text{ at the boundaries } \Omega_C \times R_*^+ \\ m(x, y, 0) &= m_0(x, y) \forall x, y \in \Psi \end{aligned} \quad (2)$$

Ω_C represents the boundaries of the domain Ψ : $\Omega_C = \Delta\Psi$. M_m is the maximum moisture absorption capacity corresponding to the relative humidity (HR) (%) imposed on the matrix domain boundaries, D stands for the diffusion coefficients of the polymer matrix; $m(x, y, t)$ is the moisture content at each time

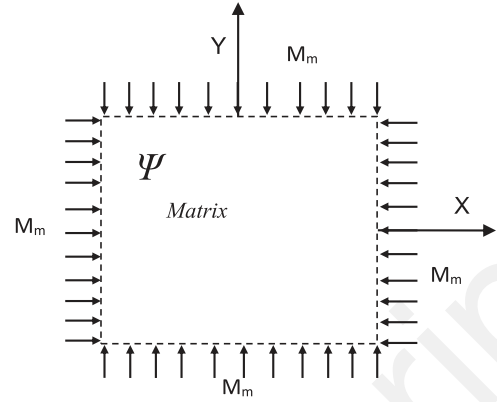


Figure 1. Undamaged matrix REV.

Table 1. Input data used for solving the diffusion problem.^{19,22,23}

Material parameters	Pure resin (Epoxy 5208)
Relative humidity (HR) (%)	80%
α	0.059
β	1
Coefficient of diffusion D_m (mm ² /s)	7.312×10^{-8}
Water vapor coefficient of diffusion in air D_a (mm ² /s)	5.9×10^{-5}
Bulk density ρ (kg/m ³)	1265
Temperature	20°C

and $m_0(x, y)$ is the initial moisture content existing in the REV at time $t=0$, which is often considered to be null. To solve problem (1) we use the finite element method, owing to the software (Comsol[®]). The parameters used for performing numerical computations are shown in Table 1.

For this resolution, equation (2) will be nondimensionalized by performing the following variable change: $\eta = \frac{x}{L}$, $\varphi = \frac{y}{L}$, $\tau = \frac{D}{L^2} t$ (where L represents the length of the REV; as a result, the dimensions of the REV become equal to 1×1 instead of $L \times L$).

Figure 2(a) shows the distribution of moisture content obtained during transient stage of the diffusion process. Indeed, the center of the REV is not yet saturated compared to the area close to the boundaries. In Figure 2(b), the REV has attained permanent stage: the moisture content is uniform and corresponds to the moisture content imposed at the boundaries. In this case, one can consider that the matrix is in thermodynamic equilibrium with its surrounding environment. This solution has been obtained under the assumption that the matrix presents an ideal microstructure. In reality, this structure is often far to be

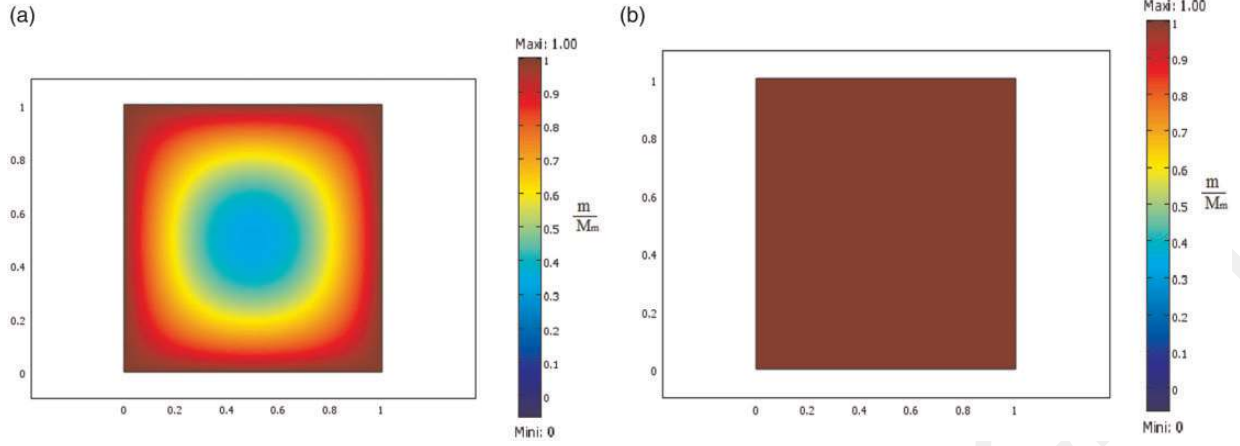


Figure 2. Moisture content distribution in undamaged matrix: (a) transient stage and (b) permanent stage (saturation).

ideal: micro-cavities in the form of porosities are reported to exist in polymer matrix and in their composites due to manufacturing process.^{2,24-31} It is conventional to define porosity as the property of a medium to contain voids at the microstructural scale. It is often described by a volume fraction expressed by the ratio between the sum of the volumes of these voids and the total volume of the medium. The authors cited above report in their work that for small volume fractions of porosities (<1%), the hygro-mechanical properties are not significantly affected. On contrary, for higher porosity levels, the effective properties of the material may be significantly affected. For the polymer matrixes and their composites, two types of porosities can be distinguished: the open type, communicating with the outer faces of the material and those closed which are far from the outer faces and located inside of the material. In addition, the work of Wisnom et al.³² highlights the possible initiation of cracks from porosities as soon as their lengths exceed a certain threshold.

The study is specifically focused on two types of cavities, depending on whether the cavity is located inside the material or opens out. Theoretical work on the modeling of the diffusion behavior of composites in the presence of porosity predicts a significant modification of this behavior.^{17,33,34} Similarly, the experimental work conducted by Costa et al.^{35,36} reveals increasing levels of saturation with the porosity rate. In what follows, we will solve the diffusive problem in the presence of damage in the form of porosity.

Diffusion in damaged matrix

In this case, we consider that the representative REV of the damaged medium consists in an elliptical cavity embedded in an infinite medium, which represents the

polymer matrix Figure 3. On the edges of this REV is imposed the maximum moisture absorption capacity corresponding to the relative humidity (HR) (%) of the surrounding environment. Initially, the moisture diffuses into the matrix then into the cavity, which is assumed unsaturated, filled with dry air. In the matrix, diffusion is supposed to be governed by Fick's law^{37,38} under the assumption that the diffusion of moisture in the hydrophilic matrix is considered independent of the mechanical state. In this case, the REV is supposed to be constituted by two phases: the matrix and the cavity. The cellular problem of diffusion to solve in the REV is defined by the following system of dimensionless equations

$$\begin{cases} \frac{\partial m(\eta, \phi, \tau)}{\partial \tau} = D\Delta m(\eta, \phi, \tau) & \text{in each phase } \Psi \times \mathbb{R}_*^+ \\ \frac{m(\eta, \phi, \tau)}{M_m} = 1 & \text{at matrix boundaries } \Omega_C \times \mathbb{R}_*^+ \\ m_r(\eta, \phi, \tau) = \bar{X} & \text{at cavity/matrix interface} \\ m(\eta, \phi, 0) = \frac{m_0(\eta, \phi)}{M_m} & \forall x, y \in \Psi \end{cases} \quad (3)$$

Problem resolution in the case of the damaged matrix

To solve the problem, we used Comsol[®] software. In this case, the dimensions of the REV and the diffusion parameters correspond to those of the undamaged matrix (see Table 1). The diffusion coefficient in the cavity is taken equal to that of diffusion of the moisture in air, that is approximately 1000 times that of the matrix (see Table 1), since the diffusion of humidity in the air is very fast compared to the diffusion of

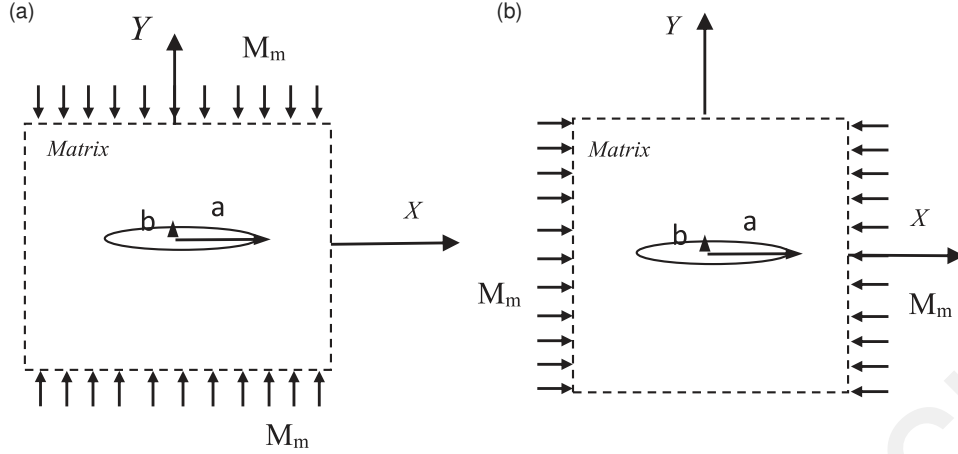


Figure 3. REV relative to the damaged medium: (a) unidirectional diffusion according to X-axis only and (b) according to Y-axis only.

moisture in a dense material. The volume fraction of this cavity is taken equal to 5% of the REV, this value is close to the limit value of the porosity rate or micro-cracks in high performance composites.³⁹ The geometrical shape of the cavity is expressed by the parameter λ , which represents the ratio between the two axes (minor axis and major axis) of the ellipse that represents the cavity. In this work, we consider three geometrical shapes for the cavity, depending on whether the cavity has a flattened shape, corresponding to low values of λ , either a convex shape, relative to mean values of λ , as well as the limiting case of a sphere, corresponding to λ equal to 1.

Determination of the moisture content at the matrix/cavity interface

We assume that the cavity is filled with air and we reason in terms of its relative humidity. This relative humidity depends on the external environment: in our case, the polymer matrix surrounding the cavity. Based on the thermodynamics laws for air containing a quantity of water vapor, its specific humidity or the mixing ratio X , which is defined as the ratio of the mass of water vapor in an air element to the mass of dry air for the same element, is expressed by⁴⁰

$$X = 0.622 \times \frac{P_V}{P_{atm} - P_V} \quad (4)$$

where

$$P_V = \frac{P_{VS} \times HR}{100} \quad (5)$$

where P_{atm} , P_V , P_{VS} , X are, respectively, the atmospheric pressure, the water vapor partial pressure, the

saturation vapor pressure and the absolute humidity expressed in ($\text{kg}_{\text{eau}}/\text{kg}_{\text{airsec}}$). By replacing the vapor pressure P_V in equation (4) by expression (5), we get a new form for the absolute humidity in the cavity

$$X = 0.622 \times \frac{HR \times P_{VS}}{100 \times P_{atm} - HR \times P_{VS}} \quad (6)$$

Let us assume that at each instant a thermodynamic equilibrium is established for the moisture content in the matrix and the cavity, at the boundary of the cavity. We will assume that equation (1) remains valid in the polymer matrix at the boundary with the cavity so that we can get the corresponding relative humidity, in it by

$$HR = (M_m/\alpha)^{\frac{1}{\beta}} \quad (7)$$

By replacing the relative humidity HR by form (7) in expression (6), we obtain the relationship at the interface between the moisture content in the matrix and the absolute humidity X in the cavity. We can deduce the moisture content in the cavity, which will be denoted by \bar{X} in the following

$$\bar{X} = 0,622 \times \frac{P_{VS} \times (M_m/\alpha)^{\frac{1}{\beta}}}{100 \times P_{atm} - P_{VS} \times (M_m/\alpha)^{\frac{1}{\beta}}} \quad (8)$$

In the case where $\beta=1$, one obtains

$$\bar{X} = 0,622 \times \frac{P_{VS} \times (M_m/\alpha)}{100 \times P_{atm} - P_{VS} \times (M_m/\alpha)} \quad (9)$$

Thus, at the interface we use equation (9) for the transition from the matrix to the cavity. The saturation pressure of the saturating vapor P_{VS} at a given temperature is obtained by using the NIST Steam Tables.⁴¹ After defining all the parameters, the steps for solving the problem are summarized as follows: for each time, one must solve the diffusion problem (3) in the matrix for a given boundary condition. Then one calculates the moisture content in the cavity by equation (9).

Figure 4 shows the diffusion problem solution in the case of a flattened cavity, during the transient phase, corresponding to $\sqrt{\tau} = 0.2$ on the diffusion kinetics curve (Figure 5). Figure 4(a) displays the results obtained for a damaged matrix exposed to moisture along X-direction, whereas Figure 4(b) provides the results obtained for an undamaged matrix submitted to the same loading. Figure 4(c) and (d) displays the results obtained when the moisture loading is applied along Y-direction, for either a damaged or an undamaged matrix, respectively. In the case when moisture load corresponding to moisture content M_m is applied

in the X-direction, the moisture content at the boundary with the matrix tends rapidly to that imposed to matrix edges, since the diffusion is very fast in the crack compared to the diffusion in the matrix. However, crack reaches the saturation before the surrounding matrix. Consequently, diffusion will take place from the crack to the matrix in the transverse direction. In this situation, the saturated crack behaves then as a moisture source for the surrounding matrix see Figure 4(a). It should be noted that in this case the saturation is rapidly reached. As a first approximation, it seems that the flattened crack behaves like an additional boundary with the external environment. On the other hand, in the case of a loading according to Y-direction (Figure 4(c) and (d)), the contribution of the cavity to diffusion process is insignificant, since the edges of the cavity are far from the loading.

Figure 5 shows the evolution of the diffusion kinetics for different loading cases. We find that the evolution for the damaged matrix is similar to that of the undamaged matrix which is Fickien. We note a

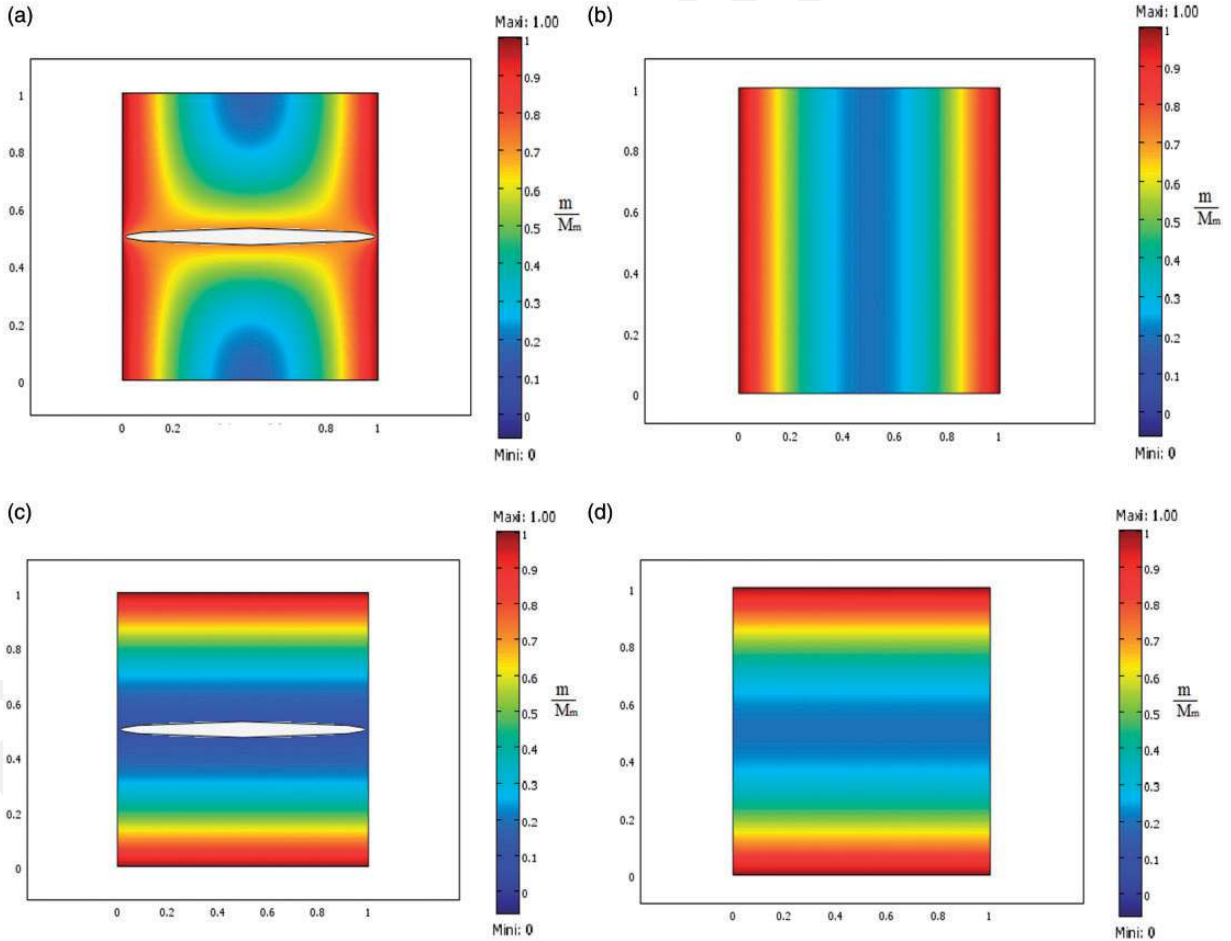


Figure 4. Problem resolution in the case of the damaged and undamaged matrix ($\lambda = 0.07$ and for crack void rate of 5%): (a,b) according to X and (c,d) according to Y, intermediate stage.

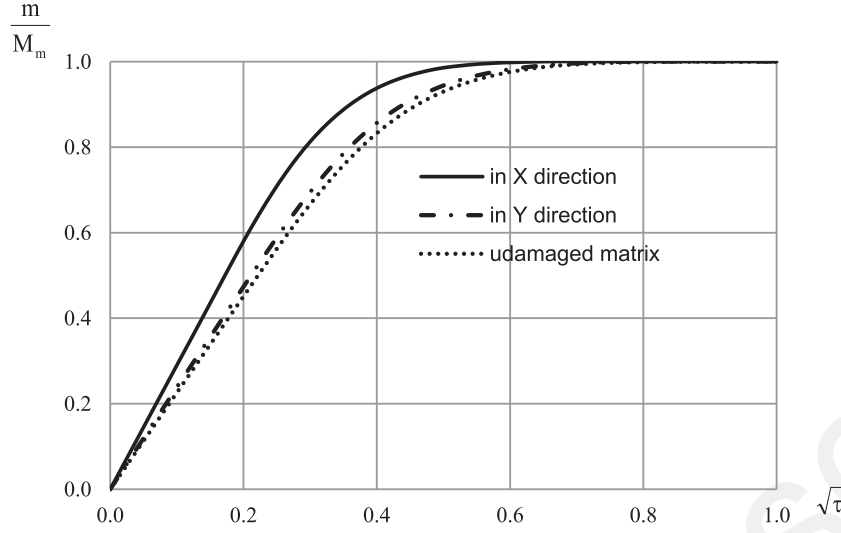


Figure 5. Diffusion kinetics evolution for the damaged matrix ($\lambda=0.07$ and cavity volume fraction of 5%).

significant difference between diffusion kinetics curve obtained in case of moisture loading in X-direction and that obtained in case of undamaged matrix. This is explained by the fact that the edges of the cavity are very close to the borders where the moisture loading is applied. On the other hand, in the case of a loading according to Y, this difference is less significant, since the cavity is far from the borders. This is illustrated by the diffusion evolution in Figure 4. Consequently, diffusion anisotropy takes place between the moisture loadings in two directions. This anisotropy is due to the fact that in the case of a hygroscopic loading next X, the cavity will quickly reach saturation as it is closer to loading. Therefore, diffusion will take place from the cavity to the surrounding environment. On the contrary, in the case of diffusion in the Y-direction, the cavity is very far from the boundaries exposed to the humid environment, so it cannot contribute to accelerate the process. On the other hand, it should be noted that the difference in moisture content at saturation between the damaged matrix and undamaged matrix is a long way from being significant. This is due to the fact that the amount of moisture (in gaseous form) captured by the cavity is very small compared to the overall matrix moisture up take.

The relative humidity evolution in cavity can be determined from equations (7) and (8)

$$HR = \frac{\bar{X} \times P_{atm} \times 100}{P_{VS} \times (\bar{X} + 0.622)} \quad (10)$$

In Figure 6, the evolution of the relative humidity in the cavity plotted in the two case of loadings gives an explanation to the difference observed in the diffusion kinetics predicted. We note in the case of a loading

according to Y, moisture took time to reach the cavity; this delay is indicated by the first part of the curve which is on the time axis at the first diffusion stage compared to the case when the loading is in the X-direction, at which the cavity is half saturated.

Determination of effective diffusion coefficients

In the following, we will determine the effective diffusion coefficient in the presence of cavity in order to quantify its influence on the equivalent macroscopic diffusive properties of the material.

Identification method

In order to determine the effective diffusion coefficients in the presence of an elliptical cavity, we use a numerical solution of the diffusion problem based on the finite element method using Comsol[®] software. The interest of the numerical solution is to determine the diffusion kinetics curve of the damaged matrix, since in this case the analytical solution is non-existent. This curve will subsequently be used in the determination of effective diffusion coefficients using an equivalent model for the damaged matrix. This model consists of an undamaged matrix supposed to have the same kinetics of diffusion of the damaged matrix (the same moisture content) Figure 7. This method is simply based on the adjustment of two curves: For unidirectional moisture loading under the assumption of a unidirectional diffusion either along X or Y, we determine D_X^{eff} or D_Y^{eff} by introducing each time the values of these coefficients in the equivalent model until the curve obtained fits the damaged matrix curve.

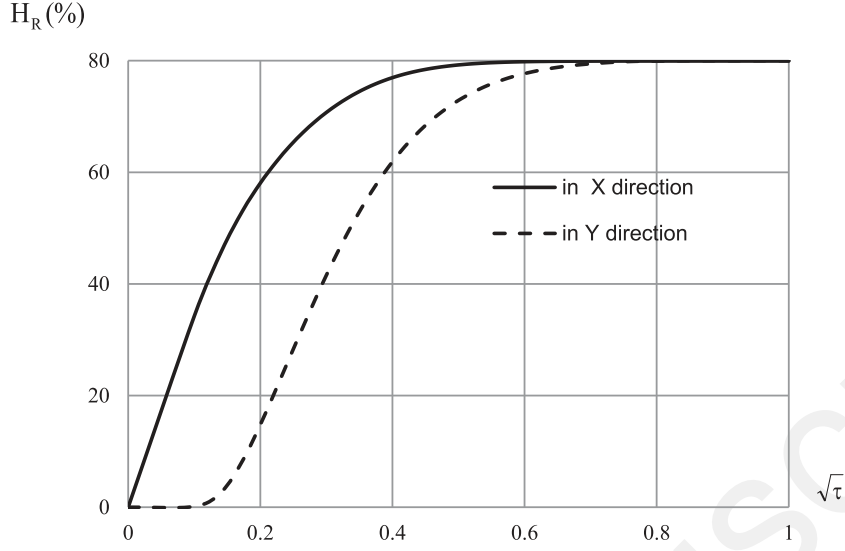


Figure 6. Evolution of the relative humidity in the cavity ($\lambda=0.07$ and void volume fraction of 5%).

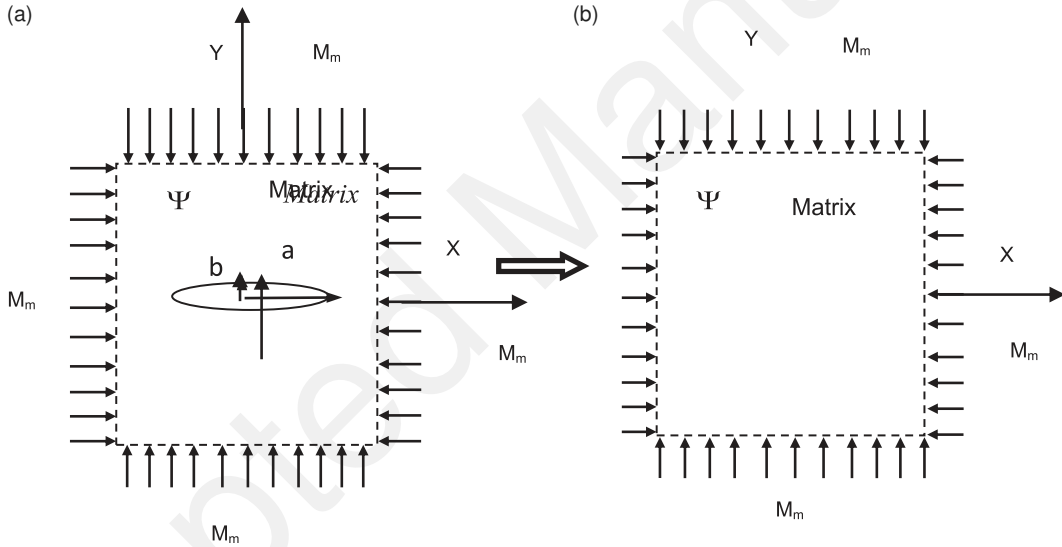


Figure 7. (a) Damaged matrix and (b) equivalent REV.

Thus, the values of D_X^{eff} and D_Y^{eff} introduced correspond to the effective diffusion coefficients. In order to obtain more precision on the effective diffusion coefficient, we use the least squares method, which can be expressed by the following equation

$$Q = \sum_i \left(m(t)_{damaged} - m(t)_{undamaged} \right)^2 < \varepsilon \quad (11)$$

where $m(t)_{damaged}$, $m(t)_{undamaged}$ are the moisture contents at time t of the damaged and that of the undamaged equivalent model, respectively, ε is a small value for acceptable discrepancy below which the adjustment of the actual model is considered to be satisfactory (11).

The diffusion anisotropy, defined by the parameter \tilde{A} will thus be determined by the ratio between the diffusion coefficients identified in the two directions, namely

$$\tilde{A} = \frac{D_X^{eff}}{D_Y^{eff}} \quad (12)$$

Then, under the assumption that the diffusion anisotropy estimated from unidirectional loading cases remains the same when the diffusion occurs simultaneously along X and Y, we will estimate the effective diffusion coefficients D_X^{eff} and D_Y^{eff} on the basis of the anisotropy ratio \tilde{A} determined beforehand when it comes to identifying the diffusive behavior

resulting from a case of loading in biaxial moisture. Since the evolution of diffusion kinetics in the damaged matrix remains Fickian, Figure 5, D_X^{eff} and D_Y^{eff} are determined using the following equation

$$\frac{\partial C}{\partial t} = D_X^{eff} \frac{\partial^2 C}{\partial x^2} + \frac{1}{A} \left(\frac{\partial^2 C}{\partial y^2} \right) \quad (13)$$

We note that these coefficients are higher than that of the undamaged matrix, even for minimal volume fractions. As predicted by the evolution of the diffusion kinetics shown in Figure 5, the diffusion coefficient in the X-direction is greater than that in the Y-direction and to that of the undamaged matrix (Figure 8). In Figure 9, anisotropy coefficient \tilde{A} has been plotted as

a function of the cavity volume fraction. This figure confirms some of the comments relating to Figure 5: the gap between the two effective diffusion coefficients increases with the cavity volume fraction. The coefficient of anisotropy thus exceeds the value of 1.6 for a cavity volume fraction of 5%.

Effect of cavity geometry on diffusion anisotropy

In this section, we study the diffusion anisotropy in the case of cavity geometric configurations described in Figure 10 and which is expressed by different values of the parameter λ . Table 2 represents the identification results for the four cavity geometric configurations shown in Figure 10.

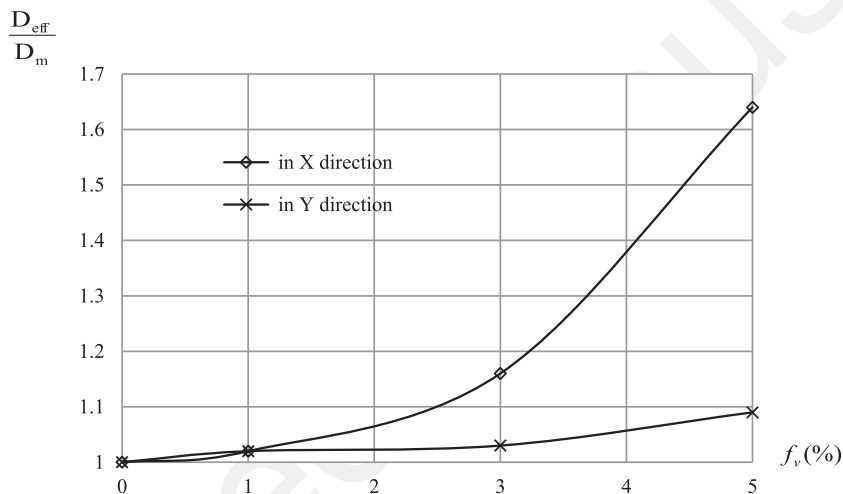


Figure 8. Effective diffusion coefficient obtained in the case of the damaged matrix by imposing uniaxial moisture loading according to X or according to Y ($\lambda = 0.07$).

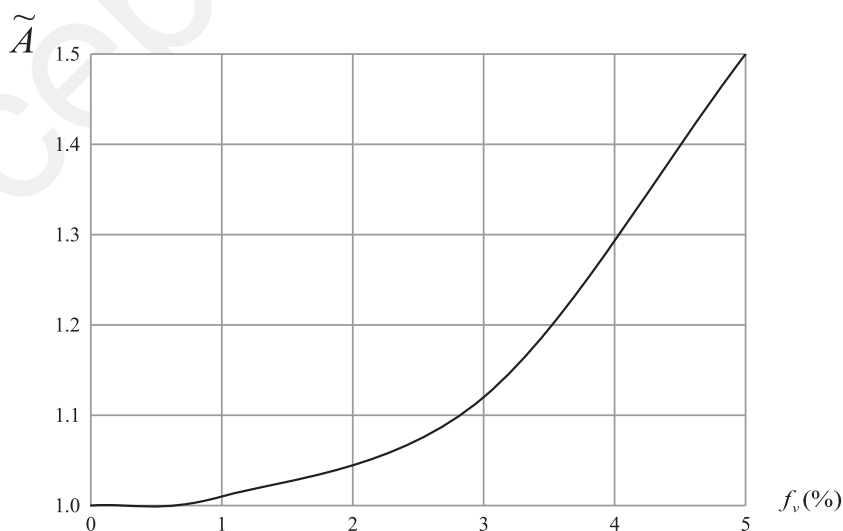


Figure 9. Anisotropy of diffusive behavior according to the crack volume fraction ($\lambda = 0.07$).

Note that the results for the three configurations ($\lambda=0.07$; 0.18 and 1), corresponding to a cavity volume fraction equal to 5%, are compared to a configuration where the cavity is extremely flattened ($\lambda=0.013$) and in which the volume fraction cannot exceed 1% for a single cavity by REV. These results shown an increase in the effect of the presence of the cavity on the diffusion expressed by diffusion anisotropy when cavity tends towards extremely flattened geometrical configurations, including minimal volume fractions. On the other hand, when the cavity tends towards convex forms, this anisotropy decreases: the diffusive behavior becomes thus isotropic in the limit case where the cavity form is a disc, the curves plotted in Figure 11 confirm these findings.

Damage modeling in case of several cavities

In the previous section of this work we are focused on damage modeling, assuming that all damage could be represented by a single cavity having a well-defined

geometric configuration and whose volume fraction is equivalent to the damage global rate. In this section, we consider here the modeling of the damage in the form of several cavities having an identical geometric configuration and occupied REV which have the same damage rate of an REV with single cavity. The material diffusive behavior anisotropy was then studied considering several cavity dispersions in the matrix, as indicated in Figure 12. In Figures 13 and 14, the diffusion kinetics curves obtained in the damaged matrix for the dispersions illustrated in Figure 12 are plotted in the case of a cavity moderate elongation corresponding to

Table 2. Identification results of effective diffusion coefficients.

$f_v(\%)$	1%	5%	5%	5%
0.013	0.07	0.18	1	1
D_X^{eff}	1.78	1.96	1.18	1.16
D_Y^{eff}	1.18	1.30	1.14	1.16
\tilde{A}	1.5	1.5	1.03	1

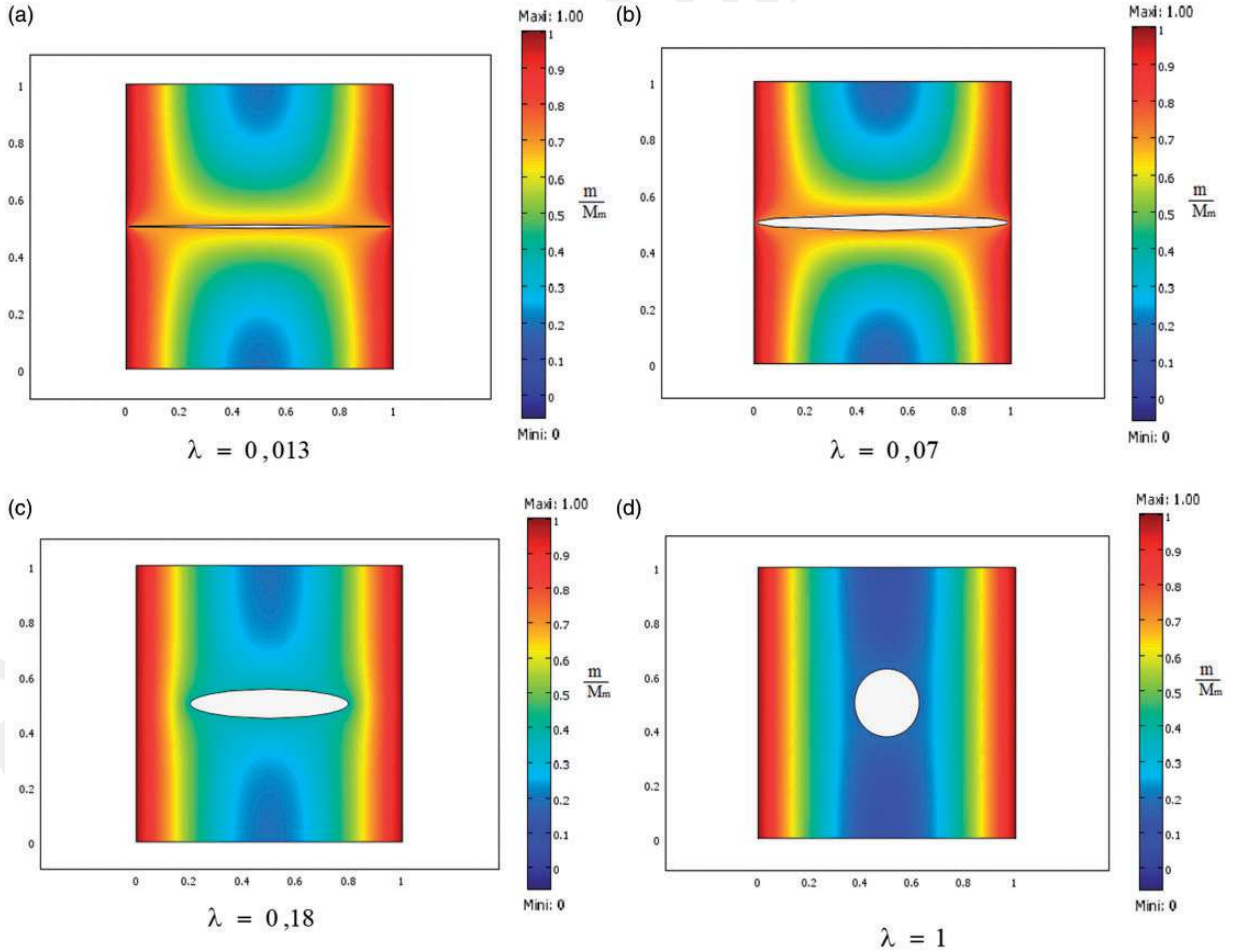


Figure 10. The moisture content for different geometric configurations of the crack during the transient regime ($\sqrt{\tau} = 0.2$).

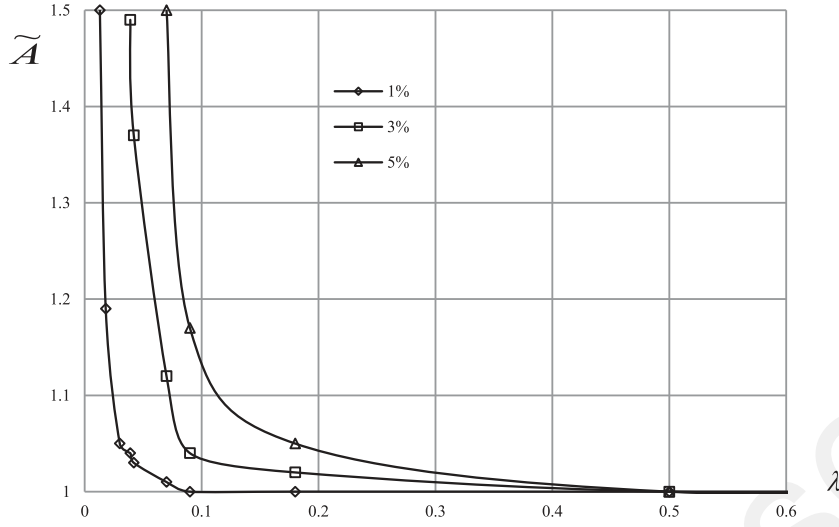


Figure 11. Anisotropy of diffusive behavior as a function of the volume fraction of damage for different cavity configurations.

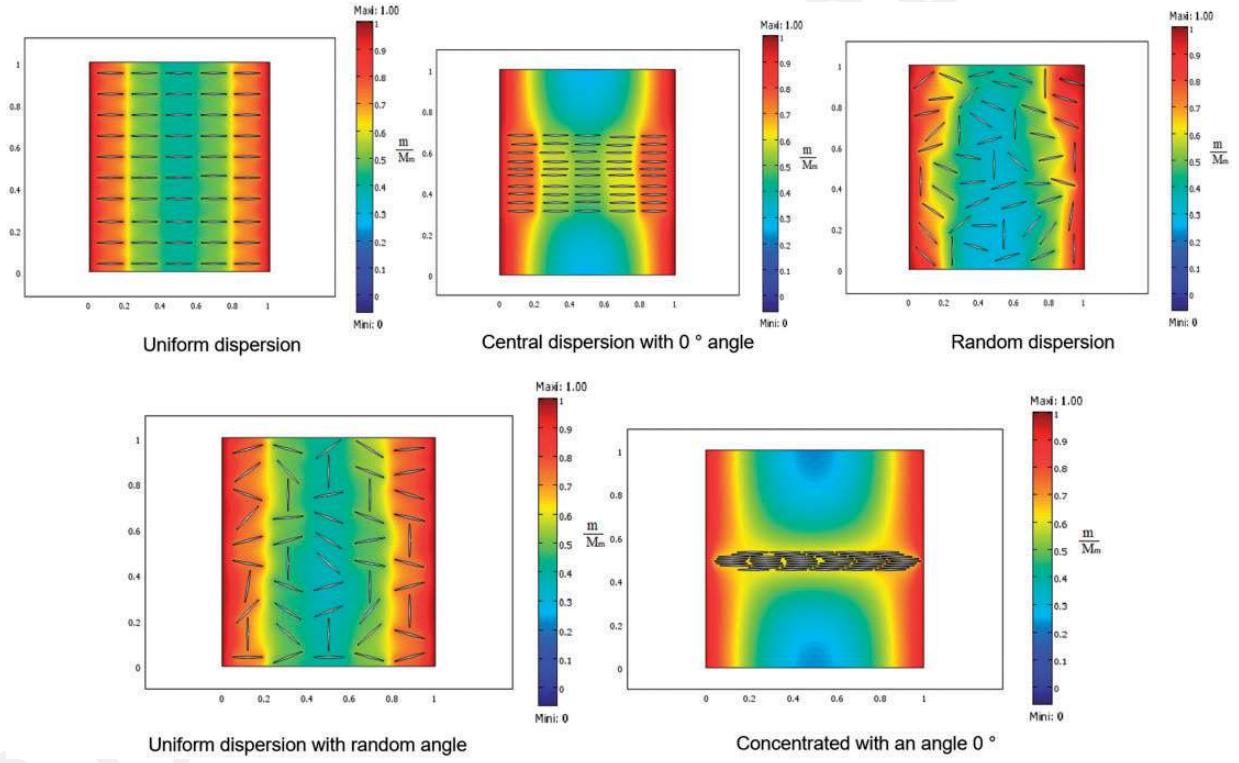


Figure 12. Transient numerical simulation of the moisture content field in a damaged matrix. Effect of the parameters taken into account to represent the distribution of cavity within the REV ($\sqrt{\tau} = 0.2$).

$\lambda = 0.07$ and in case of most pronounced elongation expressed by $\lambda = 0.013$.

For a cavity with moderate elongation, the diffusion kinetics curves for the different dispersions seem to be in agreement and are very close to that for a single cavity per REV. For a flattened cavity, we find a

significant deviation between the diffusion kinetics curves obtained by different dispersions. In this case, the diffusion kinetics curve obtained for concentrated cavities with angle 0° is the closest to that obtained for a single cavity by REV, even considering a volume fraction of 1%.

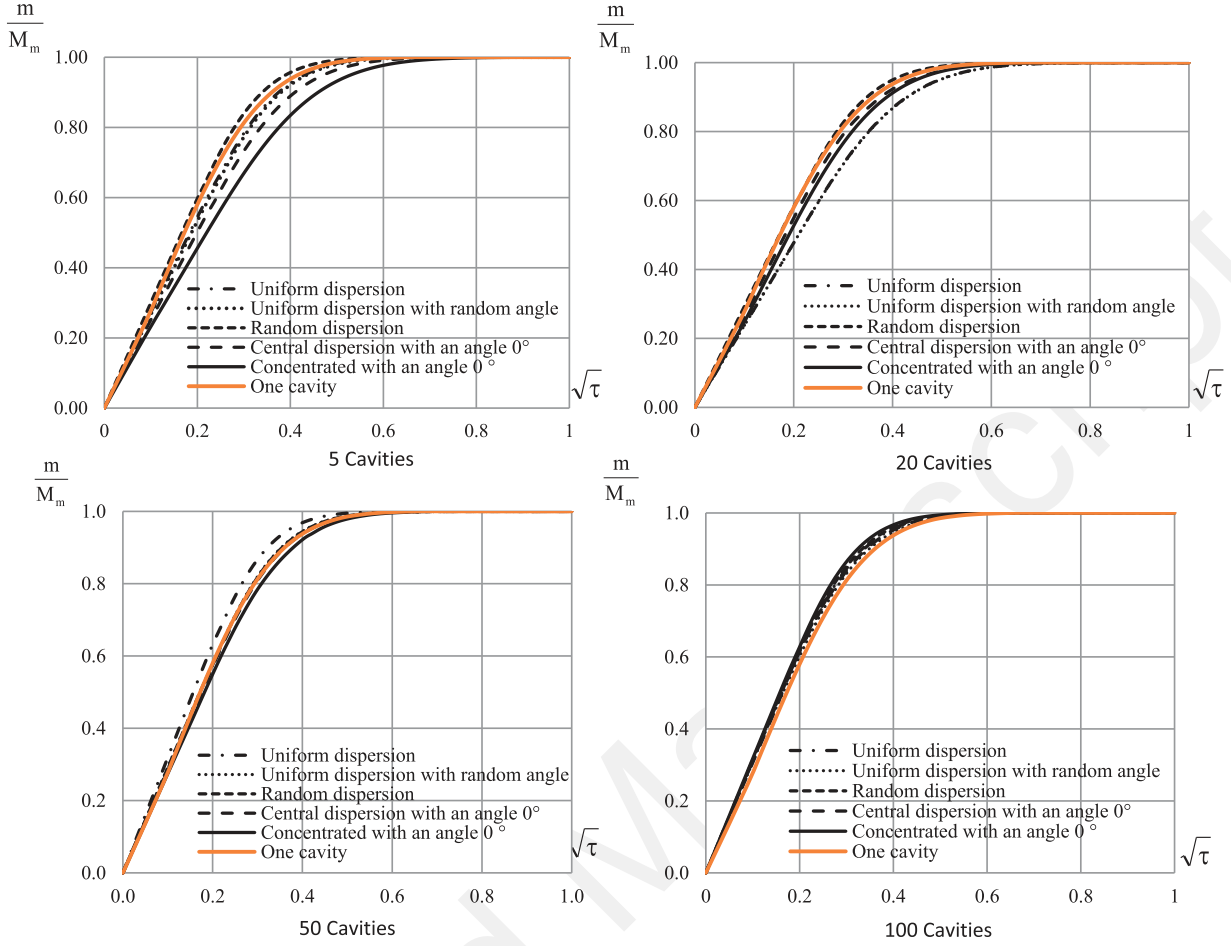


Figure 13. Diffusion kinetics evolution of damaged matrix for different distributions of cavities within the REV ($\lambda = 0.07$).

The main remark that can be drawn from these curves is that the diffusive behavior of the damaged matrix remains Fickien, whatever is the cavities number per REV and that for all the considered dispersions. In addition, we can notice, that the curves obtained are characterized by a slope which increases with the length of the cavity. In Figure 15, the diffusion behavior anisotropy is plotted versus the number of cavities per REV, for the dispersions illustrated in Figure 12. Two configurations of the flattened cavity are considered which, respectively, correspond to $\lambda = 0.07$ for a moderate elongation and $\lambda = 0.013$ for a more pronounced elongation of the cavity. The purpose of these simulations is to detect the effect on material diffusive behavior in case of the multiplicity of cavities with a similar geometrical configuration.

The curves of Figure 15(a) initially reveal a significant fluctuation of the anisotropy between the value obtained for a single cavity and the values obtained by considering an REV with several cavities.

This fluctuation tends to disappear as we increase the number of cavities inside the REV. In addition, the evolution of anisotropy seems to have increased sensitivity to cavity dispersion in the REV. For an average elongation of the cavity corresponding to $\lambda = 0.07$, and in the case of a uniform dispersion, we find that for an REV with five cavities, the anisotropy drops by nearly 30% of the predicted value in the case of a single crack. For the same dispersion, and for a larger number of cavities, there is an increase, which reaches approximately the value of 1.7 for 100 cavities per REV. For random angle dispersion, we note an anisotropy inversion in case of five cavities in REV then it returns to normal when the number of cavities increases and it reaches that of a single cavity for 100 cavities per REV. We note that for the other dispersions, the anisotropy decrease is less accentuated; however, beyond a certain number of cavities by REV, the anisotropy becomes less sensitive to the number of cavities and that obtained for different dispersions tends to converge to a single value, except in the case of a

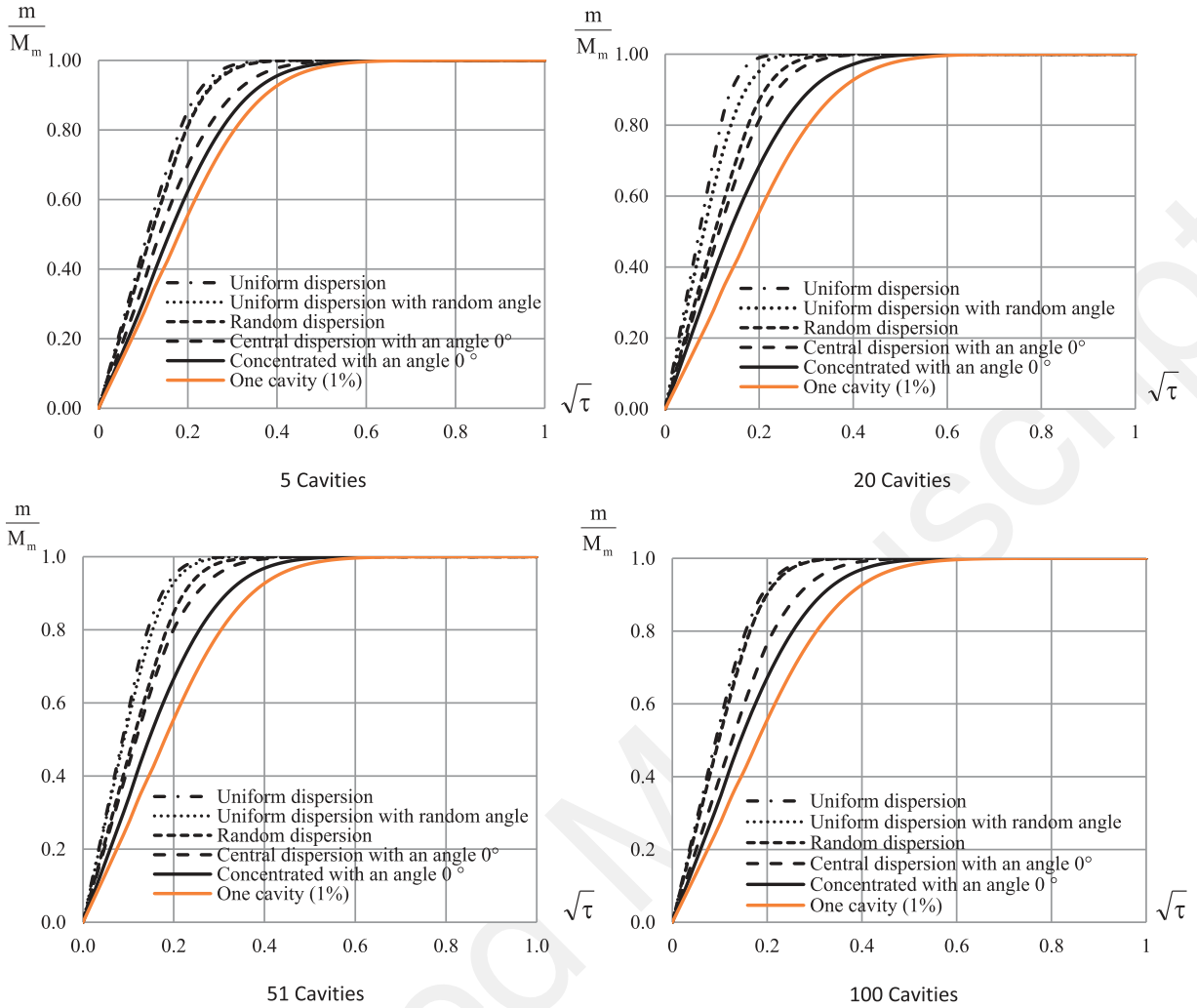


Figure 14. Evolution of the kinetics of diffusion for a damaged matrix for different distributions of cavities within the REV ($\lambda = 0.013$).

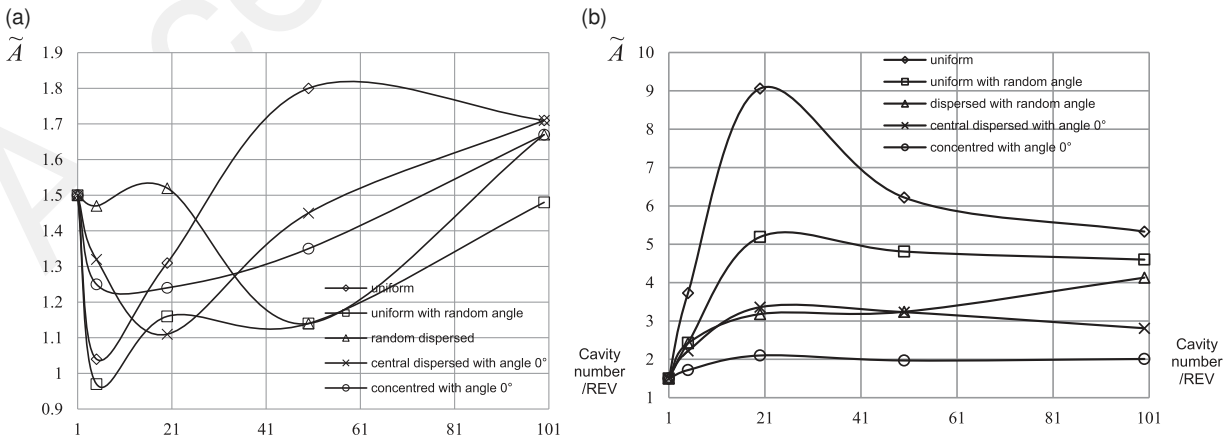


Figure 15. The diffusive behavior anisotropy versus crack number by REV: (a) $\lambda = 0.07$ and (b) $\lambda = 0.013$.

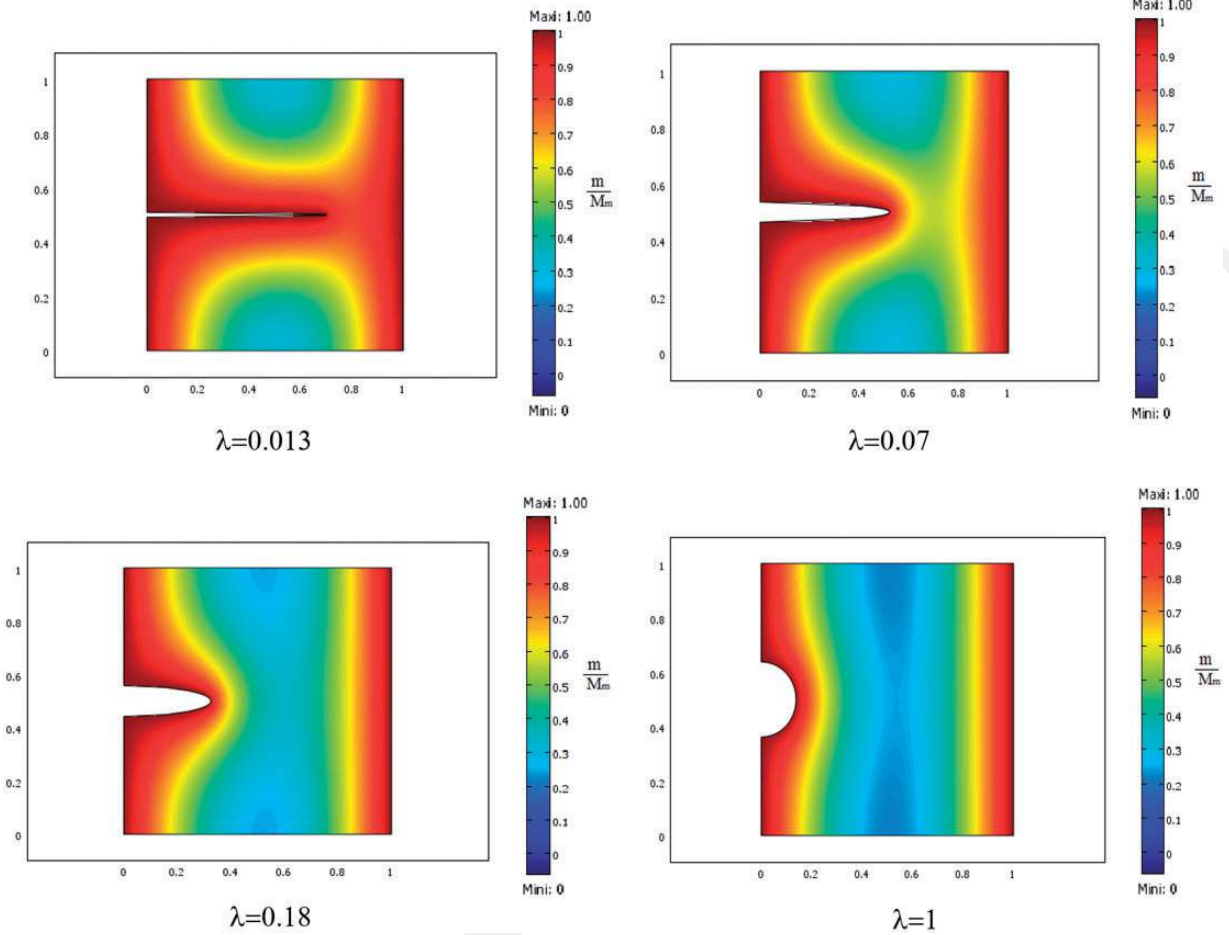


Figure 16. Moisture content profile in a polymer sample with open cavities of various shapes ($\sqrt{\tau} = 0.2$).

uniform dispersion with a random angle where it becomes close to anisotropy obtained in the case of single cavity.

This value differs according to the dispersion. The coefficient of anisotropy then decreases and all the dispersions tend to get closer. Nevertheless, the difference between them remains very important even for 100 cavities per REV. For this number of cavities, the maximum of the anisotropy is comparable to the case of a uniform dispersion. On the other hand, the minima corresponds to that of a dispersion concentrated at an angle of 0° and which approaches the anisotropy obtained for a single crack by REV. In Figure 15 (b) is illustrated the evolution of diffusion anisotropy as a function of cavity dispersion within the REV for a form factor $\lambda = 0.013$. In this case, the anisotropy evolution of the diffusive behavior presents minima for an REV with a single cavity. Then, very large fluctuations of the anisotropy coefficient occur with the increase of the number of cavities in the REV. The anisotropy coefficient maximum is obtained for all REV cavities dispersions and differs according to the dispersions.

The maximum that exceeds slightly nine is reached for a uniform dispersion.

Case of open cavities

Let us consider here the diffusion in case of a polymer matrix containing an open cavity. In this case, the cavity starts at one of the boundaries of the REV and extends inside it as shown in Figure 16. As part of the modeling of the moisture diffusion process in case of materials containing emerging cavities, the boundary condition applied on cavity boundaries is the same as that imposed on matrix REV boundaries.^{14,42-44} Figure 17 shows the diffusion kinetics predicted for a damaged matrix sample, as a function of the shape of an open cavity. Diffusion rate is significantly affected in the case of flattened cavity, by comparison with other cavity geometrical configurations.

Diffusion rate decreases when the cavity geometry tends towards that of a disc. For a cavity volume fraction equal to 1%, the rate of the diffusion kinetics for flattened cavity exceeds all the diffusion

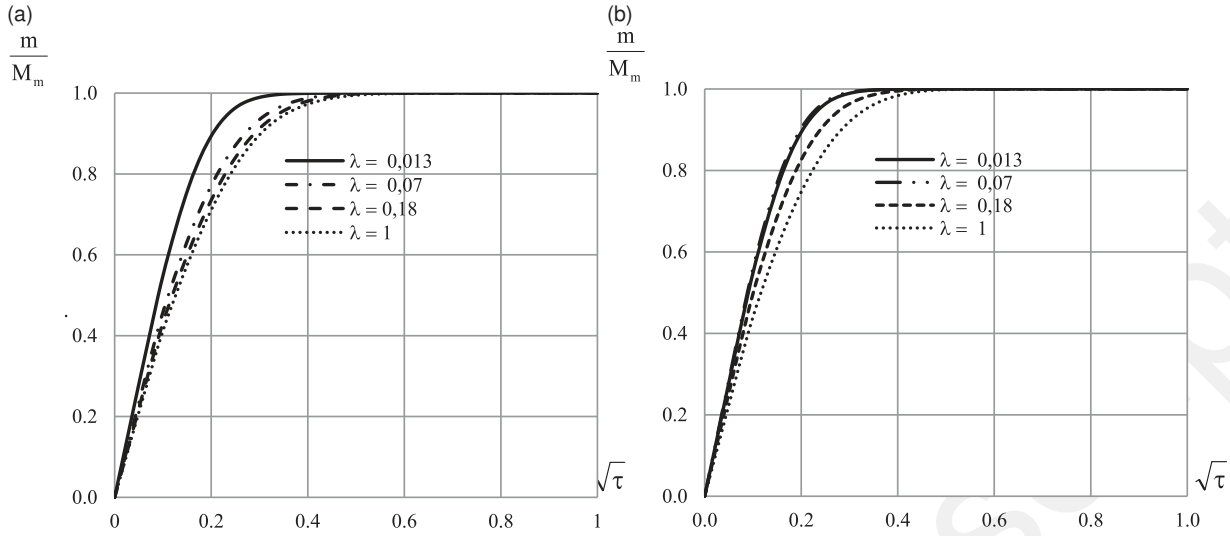


Figure 17. Diffusion kinetics evolution for a damaged matrix for different cavity geometrical configurations: (a) $f_v = 1\%$ and (b) $f_v = 5\%$.

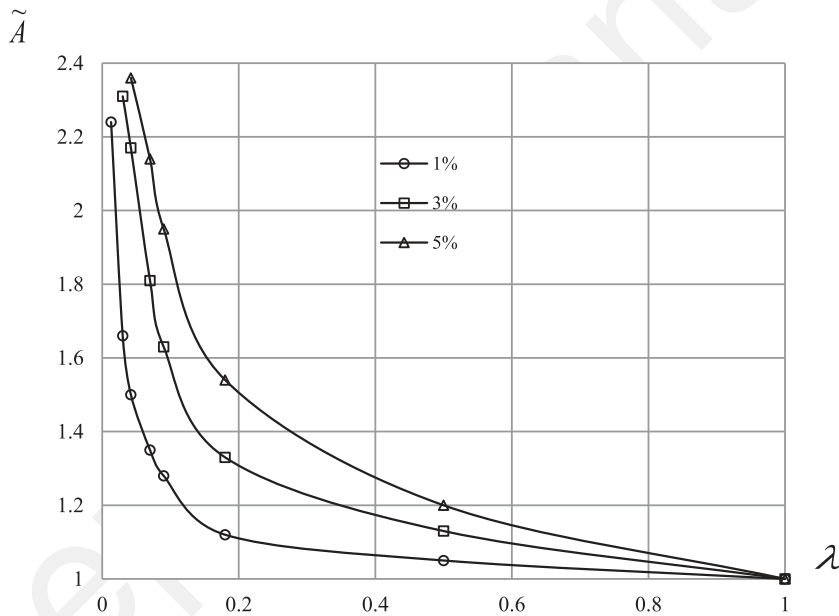


Figure 18. Evolution of the diffusion anisotropy as a function of the volume fraction and shape of an open cavity.

rate of the kinetics predicted for the others geometries considered for the cavity, even in the case when a significantly higher cavity volume fraction is accounted for (5%).

Figure 18 shows the anisotropy of diffusive behavior as a function of the volume fraction of the cavity and its geometrical configuration. Note that the anisotropy is calculated by following the same approach as for a cavity in the shape of a disk.

We can see that this anisotropy differs considerably depending on the geometry of the cavity. It reaches considerable values for flattened forms of cavity, even

for small volume fractions, whereas it tends to disappear as the cavity becomes more and more convex (when its shape becomes close to that of a disc).

Figure 19 shows a comparison between the diffusive behavior anisotropy predicted in the case of an internal closed cavity and that of an open one. This comparison shows significant discrepancies even for small volume fractions, in the case of cavities presenting a flattened shape. This deviation between the calculated anisotropy coefficients is always important when the cavity takes a convex shape, but it decreases when the cavity geometry tends towards a disc shape.

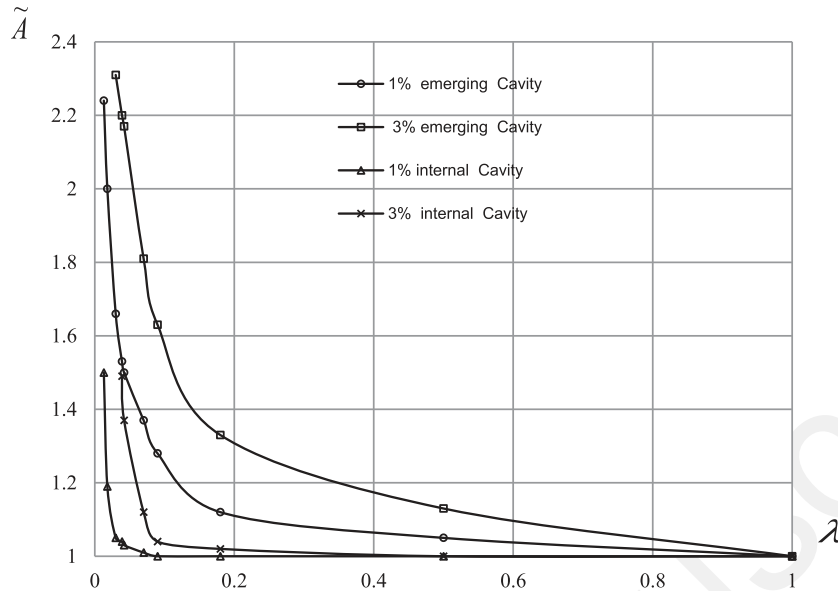


Figure 19. Comparison of the anisotropy evolution in the case of an open cavity to the internal closed cavity.

Conclusion

This work deals with the problem of moisture diffusion in a damaged polymer matrix. Diffusion in the matrix is assumed to be governed by Fick's law, whereas in the damaged area a thermodynamic approach has been implemented. Two cases were treated: the case where the damage is closed and located within the bulk of the matrix, whereas the other one deals with open cracks. Two parameters were chosen for damage modeling: its geometric configuration and its volume fraction. In the case of open cracks, several numerical examples have been treated: the case where the damage is represented by a single cavity and the configuration where the damage forms several cavities. In this last case, the effects induced by a variability of the distribution of these cavities were investigated. With a single cavity, the results obtained show a significant anisotropy of the diffusion when the cavity has a flattened shape. Moreover, this anisotropy is very sensitive to the damage volume fraction. For elongated forms of the cavity, this anisotropy tends to decrease without ever disappearing completely. In the case where the damage is represented by multiple cavities within the considered REV, fluctuations, depending on the number of cavities, were observed. However, these fluctuations disappear when the number of cavities considered exceeds a certain threshold: the anisotropy then tends to converge towards a constant value for cavity with convex shapes. However, for elongated flattened cavities, one always finds significant differences, especially when a considerable number of cracks is contained in the REV. In the case of an open crack, the results show a

significantly different behavior compared to the case of an internal closed crack.

Declaration of conflicting interests

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