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T. Peret, Alexandre Clément, Sylvain Fréour, Frédéric Jacquemin. Effect of mechanical states on water diffusion based on the free volume theory: numerical study of polymers and laminates used in marine application. Composites Part B: Engineering, 2017, 118, pp.45-66. 10.1016/j.compositesb.2017.02.046. hal-04142086

# HAL Id: hal-04142086 https://nantes-universite.hal.science/hal-04142086

Submitted on 26 Jun 2023  $\,$ 

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## Effect of mechanical states on water diffusion based on the free volume theory: numerical study of polymers and laminates used in marine application.

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## Abstract

The humid aging of composite materials is often interpreted assuming a constant diffusivity and most particularly independent on the mechanical fields. However, some experimental investigations highlight a coupling between the mechanical fields and the water diffusion in polymer based materials. In this work, this hygro-mechanical coupling is implemented through the semi-empirical free volume theory. The transient coupled problem is numerically studied using the classical finite element method. The problem is solved with the commercial code Abaqus(c). Three numerical examples, emphasizing the interest of using such models in the investigation of the aging of composites, are presented. In the two first cases, the aging of pure resin specimen, under mechanical loading, is analyzed. In the last instance, the impact of the stiff reinforcements, assumed hydrophobic, on the water absorption behavior of an uni-directional laminate is studied. Keywords: Composite materials, moisture diffusion models, Finite Element Method, strain-diffusion coupling, multi-physics, transient hygro-mechanical problem.

## 1. Introduction

Efficiency is the ultimate goal in many industrial sectors and most specifically for transport and energy. The lightest the structure is, the best are the performances. Thus, mass reduction appears as one of the main targets in structural design. Nowadays, the use of composites is growing. For instance, Glass Fiber Reinforced Polymer (GFRP) are widely used in marine and wind energy conversion industry, mainly for economical reasons, but reinforcements made of carbon may be preferred in tidal turbine blades design [1, 2]. The better specific properties of composites compared to those of conventional metallic materials [1, 3, 4, 5, 6] explain the enthusiasm in their use. Moreover, composite materials are fatigue resistant [2, 7]. Besides, they do not suffer corrosion and their maintenance is easier [6]. Furthermore, Bragg grating sensors

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can be incorporated into the material during manufacturing in order to monitor, in real time, internal strains [8, 9, 10]. Such monitoring may reduce the required number of structural inspections [6, 7].

Although GFRP and Carbon Fiber Reinforced Polymer (CFRP) present many advantages over metallic materials in marine applications, one must be cautious. Indeed, for such materials, it is well known that the polymeric resins (polyester, epoxy, etc.), used as matrices, absorb moisture. Due to this absorption, composites are prematurely aged. In fact, the absorbed water can react (either reversibly, by plasticization or irreversibly, for instance through hydrolysis) with the polymer network [11, 12]. As a result, the mechanical properties of polymer composites may be weakened when exposed to ambient fluid. Furthermore, moisture absorption yields a hygroscopic swelling of the matrix, which, coupled to the strong heterogeneity between the properties of the matrix and those of the hydrophobic reinforcements, induces heterogeneous local internal stresses within the composite [13]. Those stresses might eventually deteriorate the matrix/reinforcement interface [14, 15]. Moreover, the latter internal stresses, added to the ones induced by external forces, may cut down the sustainability of the material [16, 17, 18], and thus, disrupt the behavior of the structure [19, 20]. It is thereby critical to perform numerical analyses to predict the long-term behavior of the structure. A lot of experimental studies have been devoted to the diffusion of water in polymeric resins and composites [21, 22, 23, 24, 25]. Most of them point out behaviors following the Fick model predictions [26] but some exhibit deviations from this classical model, that are referred as "anomalies of diffusion" [26, 27]. The modeling of these so-called anomalies of diffusion can be done using improved models such as the Langmuir one [28]. These models can be used to study the effective water diffusion behavior of a real composite structure. The involved boundary value problems can be numerically solved with the classical Finite Element Method (FEM). In [29, 30, 31, 32, 33], the authors have carried out such studies assuming constant diffusivity in the Fick and the Langmuir law to be satisfied. Another way consists in taking into account the existence of coupling effects between moisture diffusion and others physical phenomena such as chemical reactions [11] or mechanical fields [34]. This coupling, between the moisture diffusion and the strain field imposed by external mechanical loading, exists indeed in polymer [35, 36] and in composite materials [37, 34, 38, 39]. For instance, specimen subjected to tensile load absorb the water faster while those in compression have a lower water diffusivity [38, 36]. In the first studies about the free volume theory, the diffusivity was written as a function, inspired by the Doolittle equation, of the stress tensor. Recently, in [40], the diffusivity was expressed according to the strain state emphasizing that the more space is available for water molecules, the faster they move in the polymer network. In this work, the second vision is adopted (*i.e.* strain-assisted diffusion is considered), since it enables to account for hygro-mechanical effects occuring in neat resin specimens in the cases when the internal moisture field is independent from the depth (the stress field due to the hygroscopic expansion is null in this specific case).

In the present work, the dependence on the local strain field of the diffusivity, depicted in the free volume theory, was implemented in the Abaqus<sup>TM</sup> code under user-element form [41]. Simulations on homogeneous

pure resin specimen and on composite materials were performed. For the latter considered materials, the distribution of the reinforcements is usually not regular in reality [29, 30, 42] and a random generator is thus used to create irregular geometries of the microstructure when one wants to consider a high volume fraction of fibers. Two diffusion models are considered: i) the Fick law assuming a constant diffusivity, simply referred as Fick or uncoupled in the following and ii) the coupled strain assisted model, based on the free volume theory. In this paper, numerical transient uncoupled and coupled hygro-elastic analysis are carried out so as to quantify the diffusion phenomenon. The resulting time-dependent hygroscopic strain field is then used to evaluate the deformation of the material considering a linear elastic assumption.

The paper is organized as follows. Section 2 deals with the diffusion and mechanical constitutive equations. The differences between the two diffusion models are presented. Section 3 gives details concerning the discretized problem within the FEM framework and its resolution. The section 4 presents the identification process of the coupled model parameters. The section 5 is dedicated to the numerical investigations. Three distinct studies are performed. The first application simulates the aging of an epoxy resin under unidirectional traction and compression loading. The second study deals with the effect of flexural loading on the diffusion process within the same resin. Finally, the last application involves glass fibers reinforced polymer only submitted to the hygroscopic swelling. We compare the results between the uncoupled and coupled models according to local and global quantities of interest. Some concluding remarks are finally drawn in Section 6.

#### 2. Problem formulation

## 2.1. Description of the studied domain

In this paper, both homogeneous and heterogeneous materials are considered. They occupy the spatial domain  $\Omega \in \mathbb{R}^d$  with  $d \in 1, 2, 3$ , written in the heterogeneous case  $\Omega = \Omega_r \cup \Omega_m$ , where  $\Omega_m$  and  $\Omega_r$ respectively represent the matrix and the reinforcements phases. For the homogeneous case, we write  $\Omega = \Omega_m$ . The boundary  $\partial\Omega$  is made up of four parts. On  $\Gamma_c$  the environmental condition are set up, on  $\Gamma_u$ 



Figure 1: heterogeneous model problem domain.

displacements are prescribed and on  $\Gamma_s$  are applied the external forces. The last part  $\partial \Omega \setminus \{\Gamma_c \cup \Gamma_u \cup \Gamma_s\}$  is free.

#### 2.2. Diffusion problem

The moisture content  $c(\boldsymbol{x},t)$  at a material point of position  $\boldsymbol{x}$  at time t is defined by

$$c(\boldsymbol{x},t) = \frac{m_w(\boldsymbol{x},t)}{m_0(\boldsymbol{x})},\tag{1}$$

where  $m_w(\boldsymbol{x}, t)$  is the local water uptake, whereas  $m_0(\boldsymbol{x})$  is the initial mass. The spatial average moisture content  $\bar{c}(t)$  on the domain  $\Omega$  is computed from

$$\bar{c}(t) = \frac{1}{M_0} \int_{\Omega} \rho(\boldsymbol{x}) c(\boldsymbol{x}, t) \, d\Omega, \qquad (2)$$

where  $\rho(\mathbf{x})$  is the local density and  $M_0$  denotes the initial sample mass. Afterwards  $\overline{c}(t)$  also refers to the global moisture content. The latter is related to experimental data such as the mass of the sample M(t) through the following relationship

$$\bar{c}(t) = \frac{M(t) - M_0}{M_0}.$$
(3)

On the other hand, the fibers are assumed hydrophobic and the diffusion problem will be therefore solely written on  $\Omega_m$  for the heterogeneous case. Polymeric resin constitutive of the matrix is considered as a homogeneous isotropic material. The resin is assumed perfectly healthy (*i.e.* without defects) and particularly porosity is not taken into account.

#### 2.2.1. Fick diffusion model

The Fick law is a common model to represent a diffusion process where each water molecule is free to move in the polymer network associated with domain  $\Omega_m$ . Since the diffusivity is assumed constant (*i.e.* independent of moisture content or mechanical states), the Fick local diffusion problem writes: find the solution field  $c(\boldsymbol{x}, t)$  such that

$$\frac{\partial c}{\partial t} = D\Delta c \quad \text{on } \Omega_m \times T, 
c = c_{imp} \quad \text{on } \Gamma_c \times T,$$
(4)

where  $c_{imp}$  is a moisture content prescribed on a part  $\Gamma_c$  of boundary  $\partial\Omega$ . It is common to impose the maximal moisture absorption capacity  $c_{imp} = c^{\infty}$  which is experimentally attained in permanent regime when the material is submitted to the same humid environmental conditions than that considered for the numerical simulations.

#### 2.2.2. Free volume theory

The Fickean model assuming a constant diffusivity is widely used in numerical computations [13, 19, 33], mainly due to the similarity with the Fourier thermal conduction problem already implemented in most of industrial finite element codes. However, in the 80's, experimental works alwe been published, emphasizing a dependence of the diffusivity on the mechanical field, for both pure resin and composite samples [35, 36, 37, 34, 39]. The authors highlight the coupling between the diffusion kinetics and the mechanical states, by performing aging tests under mechanical loads. They emphasize a non-linear relationship between the applied stresses and effective or global (macroscopic) diffusivity of the studied samples. More recently, the coupling was expressed not using the stress tensor  $\boldsymbol{\sigma}$  but the strain  $\boldsymbol{\varepsilon}$ , instead [40]. This choice implies that the mobility of water molecules, in the polymer network, is physically related to the space available embodied by the free volume  $V_f$ . This volume, in blue on figure 2, is defined as the difference between the macroscopic observable volume V and the real volume occupied by the polymer molecules  $V_p$  (colored in red on figure 2). Assuming that the diffusivity is related to the free volume by the Doolittle equation



Figure 2: Definition of the free volume in a neat resin specimen. The black border denotes the outer surface of the sample, the red areas are the regions occupied by the polymer, whereas the blue areas denote the free volume existing between the polymer molecules.

[35, 40], the ratio between the diffusivity  $D(\varepsilon, t)$  of the polymer in a given strain state and the corresponding reference value in the free of strain state  $D_0$  is expressed by

$$ln\left(\frac{D(\boldsymbol{\varepsilon},t)}{D_0}\right) = a\left(\frac{1}{v_0^f} - \frac{1}{v^f(\boldsymbol{\varepsilon},t)}\right),\tag{5}$$

where  $v_0^f$  and  $v^f(\varepsilon, t)$  are respectively the free volume fraction of the strain free and strained polymer whereas a is an empirically identified factor. In addition,  $v_0^f$  and  $v^f(\varepsilon, t)$  are related by

$$v^{f}(\boldsymbol{\varepsilon},t) = v_{0}^{f} + \frac{\Delta V(\boldsymbol{\varepsilon},t)}{V_{0}},\tag{6}$$

where  $\Delta V(\varepsilon, t)$  is the volume variation induced by the mechanical loading (stresses or strains) and  $V_0$  stands for the volume in a free of stress/strain state. Assuming small displacements, the ratio  $\frac{\Delta V(\varepsilon, t)}{V_0}$  approximates the trace of the strain tensor denoted by  $tr \varepsilon$ . Taken into account the latter elements, the equation (5) finally writes

$$D(\boldsymbol{\varepsilon}) = D_0 \exp\left(\frac{a \operatorname{tr} \boldsymbol{\varepsilon}}{v_0^f \left(v_0^f + \operatorname{tr} \boldsymbol{\varepsilon}\right)}\right).$$
(7)

Using equation (7), the Fick local diffusion problem becomes: find the solution field c(x, t) such that

$$\frac{\partial c}{\partial t} = \nabla \cdot (D(\varepsilon, t) \nabla c) \quad \text{on } \Omega_m \times T,$$

$$c = c_{imp} \qquad \text{on } \Gamma_c \times T.$$
(8)

As explained in section 3 dealing with the numerical aspects, due to the non linearity of the problem (8), the solver needs the tangential operator  $K_{tan}$  given by

$$\boldsymbol{K}_{tan} = \int_{\Omega} \nabla \delta c \ D(\boldsymbol{\varepsilon}, t) \ \nabla \partial c \ d\Omega + \int_{\Omega} \nabla \delta c \ \frac{\partial D(\boldsymbol{\varepsilon}, t)}{\partial tr \, \boldsymbol{\varepsilon}} \ tr \ \partial \boldsymbol{\varepsilon} \ \nabla c \ d\Omega \tag{9}$$

where

$$\frac{\partial D(\boldsymbol{\varepsilon},t)}{\partial tr\,\boldsymbol{\varepsilon}} = \frac{a\,v_0^{f^2}}{(v_0^{f^2} + v_0^f\,tr\,\boldsymbol{\varepsilon})^2}\,D(\boldsymbol{\varepsilon},t).\tag{10}$$

In fact, the maximal moisture absorption capacity  $c^{\infty}(\varepsilon, t)$  also depends on the local strain  $\varepsilon$  [38, 40], according to

$$c^{\infty}(\varepsilon, t) = c_0^{\infty} + \frac{\rho_w}{\rho_p} \operatorname{tr} \varepsilon, \qquad (11)$$

where  $c_0^{\infty}$  is the maximal moisture absorption capacity of the free of strain polymer,  $\rho_w$  and  $\rho_p$  respectively represent water and polymer densities. This second coupling is more difficult to take into account in the Finite Element framework and is not considered in this work but will be implemented in further works. From now on, Fick or uncoupled refer to the diffusion problem assuming a constant diffusivity while coupled or FVT stand for the Free Volume Theory based model.

## 2.3. Mechanical problem

Concerning the deformation of the material submitted to local moisture content  $c(\boldsymbol{x},t)$  that occupies the domain  $\Omega$  under small perturbations theory, plane strain assumption is retained. We denote by  $\boldsymbol{u}(\boldsymbol{x},t)$ the displacement field, by  $\boldsymbol{\varepsilon}(\boldsymbol{u}(\boldsymbol{x},t))$  the strain tensor, and by  $\boldsymbol{\sigma}(\boldsymbol{x},t)$  the Cauchy stress tensor. Both reinforcements and matrix are assumed to be linear isotropic elastic materials represented by the fourth order elasticity tensor  $\mathbb{C}$  verifying

$$\mathbb{C}(\boldsymbol{x}) = \begin{cases} \mathbb{C}_m & \text{if } \boldsymbol{x} \in \Omega_m \\ \mathbb{C}_r & \text{if } \boldsymbol{x} \in \Omega_r \end{cases},$$
(12)

where  $\mathbb{C}_m$  and  $\mathbb{C}_r$  are constant tensors. While the mechanical properties such as Young modulus are actually moisture dependent [43] due to plasticization effects, this aspect is not treated yet in the present work. Moreover,  $\beta_h$  is the constant hygroscopic expansion coefficient which is considered, in this work, identical in each direction. The hygroscopic expansion is represented by the diagonal tensor  $\beta_h$  whose diagonal components are equal to  $\beta_h$ .  $\beta_h$  is obviously taken equal to 0 for the hydrophobic reinforcements. Finally, the quasi-static linear elastic problem writes: find, at a given time t, the displacement field u(x, t) such that

$$\nabla \cdot \boldsymbol{\sigma} = \boldsymbol{0} \qquad on \ \Omega,$$
  

$$\boldsymbol{\sigma} = \mathbb{C} : [\boldsymbol{\varepsilon} - \boldsymbol{\beta}_h c] \quad on \ \Omega,$$
  

$$\boldsymbol{u} = \boldsymbol{u}_{imp} \qquad on \ \Gamma_u,$$
  

$$\boldsymbol{\sigma} \cdot \boldsymbol{n} = \boldsymbol{f}_{imp}^s \qquad on \ \Gamma_s,$$
(13)

where  $\boldsymbol{u}_{imp}$  is the imposed displacement on the part  $\Gamma_u$  of  $\partial\Omega$ ,  $\boldsymbol{f}_{imp}^s$  is the surface load imposed on  $\Gamma_s$  and  $c(\boldsymbol{x},t)$  is the solution field of either problem (4) or problem (8).

#### 3. Space and time discretizations and resolution

Uncoupled and coupled diffusion/mechanical problems are solved using the classical Finite Element Method (FEM). At the spatial level, for each model, the discretization is done using a finite element mesh composed of 3-nodes triangles associated with linear interpolation functions. At the time level, the backward Euler integration scheme is used and the increment of time at each step is computed by the Abaqus<sup>TM</sup> solver. All computations in this work were performed in less than 4 hours on a standard laptop computer. In practice, User ELement (UEL) dedicated to uncoupled and coupled problems (4) and (8) were implemented in the industrial FEM code Abaqus<sup>TM</sup> [41], enabling the use of its spatial and time solvers. The coupled problem (8) is non linear and is solved by the Newton-Raphson algorithm [44]. The UEL developed in this work, taking into account an explicit form of the tangent operator, required by the solver, is described by the equation (9).

#### 4. Identification process on homogeneous epoxy resin pure specimen

Within the uncoupled Fick problem framework, analytic solution exists, which enables the determination of the unique diffusivity from experimental data by solving an optimization problem. Unfortunately, this is not longer true when the coupled problem involving 3 material properties is employed. It is also worth noting that there is no analytic solution for the coupled problem. This section explains the steps followed to determine the material parameters of the model. The "experimental" data are created with the 1.D analytic solution, assuming a constant diffusivity  $D_F$ , of Fick diffusion problem [26].

#### 4.1. Material properties

With only one set of data, it is hard to keep or discard potential solution  $(a, v_0^f, D_0)$ . However, authors seem to agree, for a defect-free pure resin, about the value of  $v_0^f = 2.5 \%$  [35, 38]. In addition, tests results from [39] show that the parameter  $a \in [0.031; 0.036]$  for epoxy resins. Numerical studies performed in [45] showed that the diffusivity depends linearly on this parameter. Therefore, both a and  $v_f^0$  are fixed in this work and only  $D_0$  remains unknown. Figure 3 shows the evolution of  $\frac{D(\boldsymbol{\varepsilon},t)}{D_0}$  with respect to  $tr \boldsymbol{\varepsilon}$  for the two fixed parameters a = 0.033 and  $v_0^f = 0.025$ . It is worth noting that the evolution of  $D(\boldsymbol{\varepsilon},t)$  is similar



Figure 3: Relative diffusivity  $\frac{D(\boldsymbol{x},t)}{D_0}$  with respect to  $tr \, \boldsymbol{\varepsilon}$ , obtained with classical coefficients a = 0.033 and  $v_0^f = 0.025$ .

to that of  $tr \varepsilon$ . This can be explained by the fact that a higher volume leads to more free space available for the water molecules to move within the resin. The investigation of the equation (7) highlights that the ratio  $\frac{D(\varepsilon,t)}{D_0}$  is defined, physically, only when  $tr \varepsilon \in \left] -v_0^f$ ;  $+\infty \left[$ . If  $tr \varepsilon < v_0^f$ , then  $D(\varepsilon,t)$  vanishes. This is quite straightforward remembering that water molecules can only move in the free space of the polymeric network. Furthermore, mechanical properties are assumed constant. All parameters used in this section are presented in table 1.

Epoxy						
$\rho \left( Kg/m^{3} ight)$	1310 [29]		$D_F(\mu m^2/s)$	1.0		
$E\left(MPa ight)$	2700 [46]		$c^{\infty}(\%)$	3.0		
ν	0.35~[46]		a	0.033 [39]		
$\beta^h_x = \beta^h_y$	0.0025		$v_0^f$	$0.025 \ [35,  38]$		

Table 1: Mechanical and diffusion properties for the epoxy resin.

## 4.2. Geometry and boundaries

The diffusion parameters are determined on specific coupons. Those square specimen have small thickness over side length ratio  $e/l \ll 1$ . In practice, a thickness of e = 3 mm and a side length of l = 100 mm are useful. According to this geometry, water absorption by the edges can be neglected. Therefore, the diffusion problem becomes 2.D. so only the half top of the specimen is represented. Figure 4 shows the geometry and the boundaries used in simulation. The environmental condition (in blue) is imposed on the top edge. Symmetrical condition along the x-axis (in red) is imposed on the two sides while the one along the y-axis (in green) is imposed on the bottom.



Figure 4: Pure resin aging specimen scheme (a) and the geometry with the boundary conditions used in computation (b).

#### 4.3. Results and discussion

We define  $D_F^{eq}$ , the constant diffusivity obtained with an optimization process, on data from FVT diffusion problem simulations. In order to determine the initial diffusivity  $D_0$  in coupled problem, the idea is to perform some computations with different  $D_0$  and plot the evolution of  $D_F^{eq} = f(D_0)$ , where f is a prior unknown function.  $D_0$  is a solution of the following equation

$$f(D) = D_F. (14)$$

Presuming that f is both a continuous and a monotonic function, the higher  $D_0$  the higher  $D_F^{eq}$ . Thus, it is possible to mark off  $D_0 \in [D_0^m; D_0^M]$ , where  $D_0^m = D_F \exp\left[-\frac{a \operatorname{tr} \boldsymbol{\varepsilon}^{\infty}}{v_0^f (v_0^f + \operatorname{tr} \boldsymbol{\varepsilon}^{\infty})}\right]$  and  $D_0^M = D_F$  with  $\operatorname{tr} \boldsymbol{\varepsilon}^{\infty} = 2\beta^h c^{\infty}$ . Using properties in table 1, we found  $D_0^m = 0.63 \,\mu m^2/s$  and  $D_0^M = 1.0 \,\mu m^2/s$ . Five computations were performed to describe f and, then, attempt to determine  $D_0$ . The sorption curves are

$D_0 \; (\mu m^2/s)$	$D_F^{eq}~(\mu m^2/s)$
(×) 0.6	0.87
(*) 0.7	1.01
(□) 0.8	1.15
(0) 0.9	1.29
$(\triangle)$ 1.0	1.43

Table 2: Equivalent diffusivity  $D_F^{eq}$  for several initial diffusivity  $D_0$ .

plotted on figure 5, where : (-) represents the assumed "experimental" data obtained with the Fick solution corresponding to  $D_F = 1.0 \ \mu m^2/s$  whereas the other curves are obtained through numerical computations using equation (7) with (×)  $D_0 = 0.6 \ \mu m^2/s$ , (\*)  $D_0 = 0.7 \ \mu m^2/s$ , (□)  $D_0 = 0.8 \ \mu m^2/s$ , (•)  $D_0 = 0.9 \ \mu m^2/s$ and finally ( $\triangle$ )  $D_0 = 1.0 \ \mu m^2/s$ . First of all, it is worth noting that the numerical curves are Fickian. This results seems to indicate that an experimental curve that do not show strong discrepancies with typical Fick kinetics does not imply absence of coupling. Secondly, it is interesting to note that curves obtained from computations marked the "experimental" curve off therefore the optimal solution  $D_0 \in [0.6; 1.0]$ . The figure 5 showed  $D_F^{eq} = f(D_0)$ . Of interest, one can notice that, in this specific case, with fixed a = 0.033and  $v_f^0 = 0.025$ , the function f is linear with  $D_F^{eq} = 1.4365 D_0$ . So, the solution  $D_0$  is trivially found,  $D_0 = 0.696 \mu m^2/s$ . All values of  $D_F^{eq}$  are listed in table 2. Now all parameters needed to perform more



Figure 5: Evolution of the macroscopic moisture content C with respect to  $\sqrt{t}$  for several  $D_0$  according to the free volume theory (a). Equivalent diffusivity  $D_F^{eq}$  with respect to  $D_0$  (b).

complex computations are known and will be used in every following numerical examples. The next section is devoted to numerical examples, where uncoupled and coupled models are compared.

## 5. Numerical cases

#### 5.1. Humid aging under a tensile or a compression load

#### 5.1.1. Description

In the first numerical study, parallelepipedic samples aged under traction or compression mechanical loading are considered. This case is interesting because similar experimental tests have shown a hygromechanical coupling [35, 36, 38]. The effect of an external mechanical load,  $\sigma_y^{app}$ , on the global diffusivity  $D_F^{eq}$ , of FM-73 epoxy specimens is showed on figure 6. The length of the specimen is 100 mm. In this work, two mechanical boundaries are considered. The first condition consisted in setting the displacement up while in the second case the force is applied on the top of the specimen. The figure 7 presents the scheme of the force imposed testing. The expected results are not the same, as in the first study the swelling of the specimen is constrained along the y direction. Due to symmetrical considerations, only one half of the coupons is depicted in the numerical computations, which are divided in two steps. In the first step, forces



Figure 6: Effect of an external load  $\sigma_y^{app}$  on the diffusivity  $D_F^{eq}$  of FM-73 epoxy specimens [36].



Figure 7: Scheme of the traction test.

or displacements are prescribed on  $\Gamma_u$  or  $\Gamma_s$  Then, the maximal moisture content  $c^{\infty}$  is applied on  $\Gamma_c$ . In the following, t = 0 corresponds to the immersion time.

#### 5.1.2. Results

We denote by  $\overline{\sigma_{yy}}(t)$  the average global stress along the y axis within the specimen and by  $\overline{\sigma_{yy}}(0)$  the average stress, along the y axis, imposed by the mechanical load. Figure 8 illustrates, for the two types of boundary conditions, the resulting time dependent evolution of the ratio  $\overline{\sigma_{yy}}(t)/\overline{\sigma_{yy}}(0)$ . On figure 8 is also depicted the evolution of the ratio  $U_y(t)/U_y(0)$  where  $U_y(t)$  is the displacement along the y axis and  $U_y(0)$  is the displacement generated by the mechanical load. As expected, when the force is prescribed ( $\circ$ ), the stress is constant. On the contrary, when the displacement is imposed ( $\Box$ ), the stress relaxes during the moisture absorption. Reciprocally, the displacement of the top surface increases when the force is imposed and remains constant in the other case. Those results seem to indicate that the kind of boundary conditions probably



influences the water diffusion behavior observed during experimental investigations. To study this effect,

Figure 8: Evolution of  $\overline{\sigma_{yy}}(t)/\overline{\sigma_{yy}}(0)$  (a) and of  $U_y(t)/U_y(0)$  (b) with respect to time t for either applied force ( $\circ$ ) or applied displacement ( $\Box$ ) boundary conditions.

we applied several displacements or forces to scan both compression and traction states. All studied cases are listed in table 3. Figure 9 shows the sorption curves obtained for those different intensities of prescribed boundary conditions. For both types of prescribed mechanical boundary conditions, lower diffusivity were observed in compression, whereas, reciprocally, traction yielded faster water absorption. Those results are consistent with literature experimental data [34, 36]. We denote respectively by  $\varepsilon_{yy}^{app}$  and  $\sigma_{yy}^{app}$ , the strain or the stress, within the specimen, generated by prescribed displacements or forces. The ratio  $D_F^{eq}/D_F$  with respect to  $\varepsilon_{yy}^{app}$  and  $\sigma_{yy}^{app}$  are also plotted on figure 10. It may be noticed that the curves are asymmetric, thus

$U_y^{imp}$	$D_F^{eq}/D_F$	$\sigma_{yy}^{imp}$	$D_F^{eq}/D_F$
$-2.5~(\triangle)$	0.19	$-120 (\diamond)$	0.47
-1.0 (0)	0.74	$-50~(\triangle)$	0.81
$-0.5 (\Box)$	0.88	$-10~(\circ)$	0.97
$0.0~(\cdot)$	1.00	$0$ $(\cdot)$	1.00
0.5 (*)	1.10	50 (*)	1.15
1.0 (×)	1.20	100 (×)	1.27

Table 3: Data of the ratio  $D_F^{eq}/D_F$  of specimen aged under mechanical load.

pointing out the non linear effect of the external load. Those results qualitatively well reproduce literature data [36]. Moreover, a noticeable fact is that a zero prescribed displacement gives similar results than the free of stress case. Indeed, due to the disturbed hygroscopic swelling, this observation was not predictable. In order to compare the impact of the two boundary conditions on the water absorption, we plot on figure



Figure 9: Evolutions of the macroscopic moisture content C with respect to  $\sqrt{t}$  for several  $\varepsilon_y^{app}$  (a) and  $\sigma_y^{app}$  (b).



Figure 10: Evolutions of  $D_F^{eq}/D_F$  with respect to  $\varepsilon_y^{app}$  (a) and  $\sigma_y^{app}$  (b).

11, the evolutions of  $D_F^{eq}/D_F$ , with respect to the mechanical stress  $\overline{\sigma}_{yy}$  imposed in the specimen as it can be found in literature [34, 36]. It may be observed that for low loading,  $\overline{\sigma}_{yy}(0) \in [-25 MPa; +25 MPa]$ , the two boundary conditions give similar results. On the opposite, for high loads the effect is enhanced, particularly in compression, when displacement are applied. This is a consequence of the confined hygroscopic swelling. To sum up, in this first example, we study the diffusion behavior of a pure resin specimen subjected to an external traction or compression load. As already noticed in literature, diffusivity increases in traction and decreases when submitted to a compression state. In addition, we also emphasized that the type of boundary conditions prescribed has a significant impact on the predicted results. Finally, it is worth noting that we qualitatively reproduced experimental evolutions of the global diffusivity found in literature.



Figure 11: Evolutions of  $D_F^{eq}/D_F$  with respect to the mechanical stress  $\overline{\sigma}_{yy}$  imposed to the specimen, for (•) force and ( $\blacksquare$ ) displacement prescribed boundary conditions.

#### 5.2. Humid ageing under three points bending load

#### 5.2.1. Description

Now, the aging of the same resin under a three point flexural bending is discussed. The test is depicted on figure 12. Material properties are listed in table 1. Two values for the external force F are considered:  $F_1 = 5 N$  and  $F_2 = 10 N$ . The coupons are 80 mm long and 3 mm thick. The distance between the support



Figure 12: Scheme of the flexural three points bending test with the boundary conditions used in computation.

## is $d = 48 \ mm$ .

#### 5.2.2. Results

The moisture content fields  $c(\mathbf{x})$ , obtained from computations with both uncoupled and coupled model, at time t = 144,000 s, close to the middle of the specimen, are shown on figure 13. It is worth noting that for the lower force, the field is almost symmetrical as in the uncoupled case. This is no longer true for  $F_2 = 10 N$  where the field is strongly disturbed in the area under the applied force  $F_2$ . The figure 13(b) presents the gradients of  $c(\mathbf{x})$  along the thickness at two specific times t = 72,000 s and t = 720,000 s, in the middle section of the specimen. At t = 72,000 s, all coupled models lead to unsymmetrical results unlike the Fick model. Close to the saturation, the coupled model became more symmetric. As expected, on the top face, the absorption is slowed down, while the diffusivity is higher on the bottom side of the coupon. This is understandable, because the material is in a compression state close to the loaded surface and in



Figure 13: Moisture field  $c(\mathbf{x})$  under a three point flexural bending load F for both uncoupled and coupled problems (a). Moisture gradient along the thickness in the middle of the specimen for the uncoupled problem (×), coupled with  $F_1$  (\*) and coupled with  $F_2$  ( $\Box$ ) (b) at two transient time steps t = 72000 s and t = 72000 s.

tension on the other side. The local diffusivity  $D(\varepsilon, t)$ , at  $t = 360,000 \, s$ ,  $t = 720,000 \, s$  and at saturation, for  $F_2 = 10 \, N$ , is drawn on figure 14. The area where  $D(\varepsilon, t) > D_F$  are colored. According to figure 14, at t = 360,000, s,  $D(\varepsilon, t)$  was predicted to remain lower than  $D_F$  in the largest part of the specimen. Furthermore, the asymmetry appeared clearly. At  $t = 720,000 \, s$ ,  $D(\varepsilon, t)$  remains lower only in a tiny area under the application point of F. The foreseeable impact of both model and force intensity on local fields is thus emphasized. Those observations may be extrapolated to high dimensions immersed structures such as tidal blades. In such structures, due to external loads, moisture fields are heterogeneous, generating internal stresses which may lead to local damage and a premature deterioration. From a design point of view, simulations made at the microscopic scale are, indeed, important to understand multi-physics phenomena but, in practice, difficult to realize on full structures. Therefore, macroscopic scale is more significant in design.

Now, global information, read quantity of interest averaged on  $\Omega$ , are discussed. The computed sorption curves, for all the configurations: uncoupled (×), coupled with  $F_1$  (\*) and  $F_2$  ( $\Box$ ), are plotted on figure 15. It is interesting to notice that there was no effects of the model and the applied external force. Actually, all curves nearly superposed. This lack of effects at the macroscale is unexpected considering the results of the microscopic analysis previously made. Thus, as in the previous studies, even when strong coupling effect



Figure 14: Diffusivity field  $D(\varepsilon, t)$  at two transient time steps (a) and at saturation (b) in the case  $F_2 = 10 N$ . Areas where  $D(\varepsilon, t) > D_F$  are colored.



Figure 15: Evolution of C with respect to  $\sqrt{t}$  for the uncoupled (×) and the coupled (\*)  $F_1$  and ( $\Box$ )  $F_2$  problems.

are present at the microscopic scale, experimental data may apparently follow the fickian law (uncoupled). Due to a lack of experimental data on this specific test, this numerical result could not be confirmed yet. Those comparisons will be investigated in further works. We remind the reader about that no effects on the maximal moisture absorption capacity as well as no plasticization effects on the stiffness or the Coefficients of Moisture Expansion were taken into account in this work. Nevertheless, even with those hypotheses, we may assume that the durability of structures is different with or without coupling.

#### 5.3. Uni-directional laminate aging specimen

#### 5.3.1. Description

The water absorption behavior of an uni-directional laminate is analyzed in this last instance. This problem is already studied in the literature but only for uncoupled cases [13, 33]. The previously studied epoxy resin is here reinforced by hydrophobic glass fibers. Mechanical properties of the fibers are given in table 4 and the epoxy properties are listed in table 1. Owing to the thickness e = 0.3 mm, the moisture

absorption by the edges is not taken into account. The microstructure geometry (*i.e.* the spatial distribution of the fibers) is created from a specific tool described in [33]. The figure 16 depicts the geometry and the boundary conditions used in computations.



Figure 16: 3.D aging specimen scheme (a) and the geometry with the boundary conditions used in computations (b).

	Glass fiber
$ ho \left( Kg/m^{3} ight)$	$2540 \ [27, \ 47, \ 48]$
$E\left(MPa\right)$	$72500 \ [27, \ 47, \ 48]$
ν	$0.22 \ [47, \ 48]$
$\beta^h_x=\beta^h_y$	0

Table 4: Mechanical properties for Glass reinforcements.

The considered volume fraction of reinforcements is close to that typically used in high performance industrial laminates  $v^r = 58.8$  %. Unlike previous examples, no external load is considered in this study so the strains are only generated by the hygroscopic swelling of the resin.

#### 5.3.2. Results

On figure 17, the moisture fields  $c(\mathbf{x})$  at time  $t = 12,600 \, s$  for both uncoupled and coupled problems are presented. The hygroscopic strain  $\varepsilon^h$ , generated by the swelling of the matrix, is disturbed by stiff reinforcements resulting in a lower local strain  $\varepsilon < \varepsilon^h$  so the largest part of the matrix is then in a compression state [33]. The latter remark may explain a smaller local diffusivity  $D(\varepsilon, t) < D_F$ . Thus, the delayed moisture absorption for the FVT model, highlighted on figure 17, was predictable, by comparison with the results obtained with the classical uncoupled Fick model. Furthermore, the gap between the two models increased with the distance from the exposed surface as shown on figure 18, where the local moisture contents, for both the uncoupled and the coupled models, within the matrix, with respect to the distance to the surface, are depicted. It is worth noting that close to the surface, both models predict similar moisture



Figure 17: Moisture content fields c(x) for both uncoupled (a) and coupled (b) problems at t = 12,600 s.

contents (coupled results are slightly higher), while in the middle of the specimen, the coupled model gives lower values. Those evolutions well corroborate the observation made on the figure 17. Furthermore, to emphasize the explanation of the delay, the local diffusivity field  $D(\varepsilon, t)$  at the instant t = 12,600 s is plotted on figure 19. Colored field indicates the areas where  $D(\varepsilon, t) > D_F$ , while reciprocally dark field represents areas where  $D(\varepsilon, t) < D_F$ . We can observe that the local diffusivity is higher, regarding the Fick model, near the exposed surface because in this area the resin is not confined. On the contrary and as expected,  $D(\varepsilon, t)$  is smaller in the largest part of the matrix, where fibers clusters are localized, and more specifically in the middle of the specimen. From now on, we investigate the mechanical quantities. The Von Mises stress fields  $\sigma^M(\boldsymbol{x},t)$ , in the matrix, at the same time  $t = 12,600 \, s$  as in figure 17, are plotted on figure 20. Owing to the assumptions of a linear hygroscopic swelling (*i.e.*  $\varepsilon_{xx}^h = \varepsilon_{yy}^h = \beta^h c(x,t)$ ), identical moisture fields lead to analogous mechanical fields. This remark is corroborated by the stress fields of figure 20. Indeed, in areas close to the exposed surface, where the moisture fields are similar, no discrepancies can be observed, while in the middle of the domain, where moisture fields are clearly different (cf. figure 17), discrepancies also exist between the stress fields. As in this study we do not consider any effect of the strain field on the maximal moisture absorption capacity of the polymer, it is obvious that at saturation, both models give the same results. Introducing an evolution of the mechanical parameters with respect to  $c(\boldsymbol{x},t)$  may enhance those disparities, as shown in [40, 43, 49]. In this first part, dicrepancies, at the local microscopic scale, between coupled and uncoupled models, were highlighted. It appears interesting to verify if, unlike the previous example, discrepancies still exist at the macroscopic scale.

We finally focus on the results based on global quantities. The gap in the kinetics of water absorption, between the two models, is also emphasized on the sorption curve of the laminate plotted on figure 21.



Figure 18: Evolutions of the local moisture contents c(y, t), with respect to the distance y to the surface, for both ( $\circ$ ) uncoupled and (\*) coupled models



Figure 19:  $D(\varepsilon, t)$  field at t = 12,600 s. Colored area correspond to  $D(\varepsilon, t) > D_F$ .

An interesting fact is that those curves, and particularly the one predicted by the coupled model, seem to follow the Fick law. Moreover, the effect of the coupling (decrease of the diffusivity) appears clearly on this figure. We define  $D_F^{lam}$  and  $D_{FVT}^{lam}$  as the assumed constant equivalent diffusivities of the laminate:  $D_F^{lam} = 5.2 \, 10^{-7} mm^2/s$  and  $D_{FVT}^{lam} = 4.7 \, 10^{-7} mm^2/s$ . The coupling leads to a relative loss of 10 % for the diffusivity in this case. It is worth noting that a lower diffusivity better corroborates experimental data [30, 31]. This result strengthens the interest of such models to increase the predictions reliability of long term durability of composite materials. Moreover, this discrepancy, even low, impacts the prediction of the time needed to reach the saturation  $t_{sat} \approx 0.7 e^2/D^{lam}$  [21]. In this specific case, the gap is only 5h but for thick coupons, for example  $e = 15 \, mm$ , the difference may be greater than a year. A last remark about the sorption curve. The lack of effect on the maximal moisture content results are identical at saturation. To pursue this study at the macroscopic scale, we investigate mechanical fields. The mean Mises stress



Figure 20: Von Mises stress fields  $\sigma^M$  for both uncoupled (a) and coupled (b) problems at t = 12600 s.



Figure 21: C evolution with respect to  $\sqrt{t}$  for both uncoupled ( $\circ$ ) and coupled (\*) problems.

evolutions  $\overline{\sigma^M}(t)$ , within the matrix, are plotted on figure 22 for both models. Like the local stress fields, the contrast between the two models appeared clearly on the macroscopic level. It may be noticed that the relative gap between the two configurations did not exceed 5 %. To sum up this last numerical case, the coupling, based on the free volume theory, impacts strongly the moisture field, and in a less manner the stress state at the microscopic scale. The effects are also spread on the global behavior of the unidirectional laminate. Like in the other studies, global sorption curves seem to follow the Fick law.

#### 6. Conclusion

In this work, the classical Fick law assuming a constant diffusivity and a strain-dependent diffusivity based on the free volume theory are compared. Furthermore, the interest of taking into account such coupling



Figure 22:  $\overline{\sigma^M}(t)$  evolution with respect to t for both the uncoupled ( $\circ$ ) and the coupled (\*) problems.

is emphasized. However, it may be said that the effect of the strain field on the maximal moisture content is not taken into account but will be focused in further works. We solved both coupled and uncoupled transient hygro-elastic problems with the Finite Element Method. For this purpose, a specific element (UEL) has been implemented in Abaqus©. Three numerical studies were then achieved. In the first example we point out the effect, of the type of boundary conditions, on the water diffusion behavior of a pure epoxy specimen aged under a traction or a compression load. Secondly, we examine the impact of a three points flexural bending test on the moisture absorption of another coupon made of the same epoxy material. Finally, using a dedicated random microstructure generator, both the Fick and the Free Volume Theory diffusion models have been compared on local and global quantities. Concerning this heterogeneous case, observations on both local and global quantities have shown discrepancies between the two models during the transient part of the moisture diffusion process. On all computations we observe that the coupled model predicts fickian behavior at the macroscopic scale. This latter remark seems to indicate that an experimental sorption curve following a typical fickian law does not imply that there is no coupling. Further works will be devoted to use such diffusion-mechanical couplings in scale transition methods in order to take into account microscopic details at a higher scale in multi-level ( $FE^2$ ) computations.

## 7. Acknowledgements

The authors acknowledge the IRT Jules Verne (French Institute in Research and Technology in Advanced Manufacturing Technologies for Composite, Metallic and Hybrid Structures) and the industrial partners (ALSTOM, CETIM, DCNS and STX France) of the collaborative project ECOSAM2 (on the lightening of marine structures and super-structures), for their financial support.

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