IMPACT OF FIBERS DISTRIBUTION ON WATER ABSORPTION IN COMPOSITE MATERIALS: A MICROSCOPIC SCALE STUDY

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Keywords: Composite materials, Fick diffusion model, Langmuir diffusion model, Numerical multiphysics analysis,

Abstract
The Glass or Carbon Fibers Reinforced Polymer (GFRP/CFRP) age when they are immersed in humid environment. The study of the moisture diffusion process in composite material is crucial to predict the long-term behavior of the structure. In this work, a comparison between the Fick model and the Langmuir one, representing differently the diffusion process at the microscale, is proposed through a numerical transient uncoupled hygro-elastic analysis. Effects of random fibers distribution on both water diffusion and mechanical states are also discussed.

1. Introduction

Nowadays, composite materials made of Glass or Carbon Fibers Reinforced Polymer (GFRP/CFRP) are widespread in a lot of industrial applications due to economic and energy purposes. The marine industry is no exception. The undeniable advantages of those composite materials led to a fast expansion of these materials in transport and energy applications. Indeed, they present good specific mechanical properties leading to a mass gain which conduct to a lower fuel consumption and better efficiency. Moreover, they have good fatigue damage resistance and can be easily repaired. Although GFRP and CFRP present many advantages, it is necessary to study the aging of the composite material submitted to a humid environment, in order to predict their durability. For such material, it is known that the polymeric resin (polyester, epoxy, etc.) constituting the matrix used in GFRP is hydrophilic whereas the reinforcements can be considered as hydrophobic. Moisture absorption yields a hygroscopic swelling of the matrix which, coupled to the contrast between the mechanical properties of each phase, induces internal stresses within the composite. Those stresses are added to the ones induced by external forces leading to a decrease of the sustainability of the material, and thus disrupt the behavior of the structure. It is thereby important to quantify the hygroscopic induced stresses in order to predict the long-term behavior of the structure. In this paper, a numerical transient uncoupled hygro-elastic analysis is performed in order to quantify these phenomena. The study is performed at the microscale where the geometrical details of the heterogeneous material appear. For the considered material, the distribution of the fibers is usually not regular [1] and a random generator is thus used to create geometries of the microstructure when one wants to consider

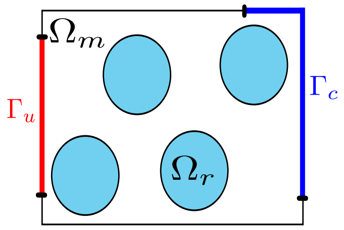


Figure 1. Model problem.

a high volume fraction of reinforcements. Two diffusion models are considered: the classical Fick's law and the Langmuir's model which assumes that absorbed moisture consists of mobile and bound phases. Such an enriched model may help to represent a wider range of diffusion processes and thus allows a better description of the investigated physical phenomena. The resulting time-dependent hygroscopic strain field is then used to evaluate the deformation of the material considering a linear elastic assumption.

2. Problem formulation

2.1. Diffusion problem

We consider an heterogeneous material, schematically depicted on figure 1, which occupies a spatial domain $\Omega = \Omega_m \cup \Omega_r \in \mathbb{R}^d$ with $d \in \{1, 2, 3\}$ and where Ω_m and Ω_r respectively represent the polymer matrix and the reinforcements. We denote by $c(\boldsymbol{x}, t)$ the moisture content of a material point, characterized by its position through vector $\boldsymbol{x}$, at time t. This moisture content $c(\boldsymbol{x}, t)$ 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 increase in mass of water and where $m_0(\boldsymbol{x})$ is the local mass at the initial time. The spatial average moisture content $\overline{c}(t)$ can be obtained with the following relation

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

where $\rho(\boldsymbol{x})$ is the local density and M_0 is the mass of the sample at initial time. In the following, $\overline{c}(t)$ will also be referred as the macroscopic moisture content. From an experimental point of view, using the knowledge on M_0 and the mass $M(t)$ at time t of the sample which occupies Ω, $\overline{c}(t)$ is evaluated using the following relationship

$$\overline{c}(t) = \frac{M(t) - M_0}{M_0} = \frac{M_w(t)}{M_0}, \tag{3}$$

where $M_w(t)$ represents the increase in mass of water within the sample with respect of M_0. From now on, all equations will be written according to the local moisture content $c(\boldsymbol{x}, t)$. In this work, we assume that the diffusion process is governed by a unique diffusion coefficient D in each spatial direction. Moreover, since the fibers are considered hydrophobic, the problem may be only formulated on the domain Ω_m. This remark is true for both models which are briefly exposed in the following.

2.1.1. Fick diffusion model [2]

The Fick law is a common model to represent a diffusion process where the all water molecules are free to move in the polymer network associated with domain Ω_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 it verifies

$$\begin{aligned} \frac{\partial\, c(\boldsymbol{x},t)}{\partial\, t} &= D\, \Delta c(\boldsymbol{x}, t) && \text{on } \Omega_m, \\ c(\boldsymbol{x}, t) &= c_{imp} && \text{on } \Gamma_c, \end{aligned} \tag{4}$$

where c_{imp} is a given moisture content applied on a part Γ_c of boundary $\partial\, \Omega$.

2.1.2. Langmuir diffusion model

In [3], the authors have proposed to divide the water molecules in two populations. The first $n(\boldsymbol{x}, t)$ is free to move while the molecules of the second phase $N(\boldsymbol{x}, t)$ are bonded to the polymer network due to reversible chemical reactions. A free water molecule could become a bonded one with a frequency α while a bonded molecule could be freed with a frequency β. The total moisture content $c(\boldsymbol{x}, t)$ naturally verifies

$$c(\boldsymbol{x}, t) = n(\boldsymbol{x}, t) + N(\boldsymbol{x}, t). \tag{5}$$

The Langmuir local diffusion problem writes: find the solution fields $n(\boldsymbol{x}, t)$ and $N(\boldsymbol{x}, t)$ such that they verify

$$\begin{aligned} \frac{\partial\, n(\boldsymbol{x},t)}{\partial\, t} + \frac{\partial\, N(\boldsymbol{x},t)}{\partial\, t} &= D\, \Delta\, n(\boldsymbol{x}, t) && \text{on } \Omega_m, \\ \frac{\partial\, N(\boldsymbol{x},t)}{\partial\, t} &= \alpha\, n(\boldsymbol{x}, t) - \beta\, N(\boldsymbol{x}, t) && \text{on } \Omega_m, \\ n(\boldsymbol{x}, t) &= n_{imp} && \text{on } \Gamma_c, \\ N(\boldsymbol{x}, t) &= N_{imp} && \text{on } \Gamma_c, \end{aligned} \tag{6}$$

where n_{imp} and N_{imp} are respectively the imposed free and bounded moisture content on Γ_c. Considering those two different populations, the Langmuir model is able to represent a wider class of diffusion phenomena. In particular, delay or, in contrary, fast absorption, at early instants of diffusion can be simulated with this model.

2.2. Mechanical problem

We focus on the analysis of the deformation of the material submitted to local moisture content $c(\boldsymbol{x}, t)$ that occupies the domain Ω under small perturbations assumption. Planes strains are assumed. We denote by $\boldsymbol{u}(\boldsymbol{x}, t)$ the displacement field, $\boldsymbol{\varepsilon}(\boldsymbol{u}(\boldsymbol{x}, t))$ the strain tensor and by $\boldsymbol{\sigma}(\boldsymbol{x}, t)$ the stress tensor. Both glass fibers and the polymeric resin are assumed to be linear isotropic elastic materials represented by the fourth order stiffness tensor $\mathbb{C}$ verifying

$$\mathbb{C}(\boldsymbol{x}) = \begin{cases} \mathbb{C}_m & \text{if } \boldsymbol{x} \in \Omega_m \\ \mathbb{C}_r & \text{if } \boldsymbol{x} \in \Omega_r \end{cases}, \tag{7}$$

where $\mathbb{C}_m$ and $\mathbb{C}_r$ are constant tensors. Moreover, we denote by β_h the hygroscopic expansion coefficient which is here considered identical in each direction. The hygroscopic expansion may be represented by a diagonal tensor $\boldsymbol{\beta}_h$ whose diagonal components are equal to β_h. β_h is equal to 0 for the hydrophobic reinforcements. Finally the quasi-static linear elastic problem writes: find the displacement field $\boldsymbol{u}(\boldsymbol{x}, t)$ such that

$$\begin{array}{rcll} div\ (\boldsymbol{\sigma}(\boldsymbol{x}, t)) & = & \boldsymbol{0} & on\ \Omega, \\ \boldsymbol{\sigma}(\boldsymbol{x}, t) & = & \mathbb{C}(\boldsymbol{x}) : [\boldsymbol{\varepsilon}(\boldsymbol{u}(\boldsymbol{x}, t)) - \boldsymbol{\beta}_h\, c(\boldsymbol{x}, t))] & on\ \Omega, \\ \boldsymbol{u}(\boldsymbol{x}, t) & = & \boldsymbol{u}_{imp} & on\ \Gamma_u, \end{array} \tag{8}$$

where $\boldsymbol{u}_{imp}$ is the imposed displacement on the part Γ_u of $\partial\Omega$, $c(\boldsymbol{x}, t)$ is the solution field of either problem (4) or problem (6).

3. Numerical aspects

3.1. Space and time discretization and resolution

Diffusion problems (4) and (6) and linear elastic problem (8) are solved using the classical Finite Element Method (FEM). At the spatial level, the discretization is done using a finite element mesh composed of 3-nodes elements associated with linear interpolation functions. At the time level, we use a backward Euler integration scheme. In practice, User Element dedicated to problems (4) and (6) were implemented in the software Abaqus^{TM} allowing the use of its spatial and time solvers. Verifications and convergence analyses, based on analytic solutions [2, 3], were carried out in order to ensure the validity of the implementation.

3.2. Generator of random geometries

A good representation of the regarded industrial materials leads to consider a high volume fraction v_r of the non penetrating reinforcements. Besides, a regular distribution of the fibers seems unlikely and a random generator is then needed to create realistic geometries of the microstructure. Generators based on a rejection process of the fibers are hard to use since the targeted volume fraction is high. We thus use a specific procedure to circumvent this issue whose starting point is a regular (*i.e.* periodic) disposition of the fibers within the microstructure. The radius of the cylindrical fibers is deterministic and only their positions are disturbed with a procedure based on elastic shocks where the radial and tangential velocities, associated with each fiber, are independent random variables. Such a technique allows obtaining the desired random geometries with low computational times.

4. Numerical applications

4.1. Material properties

The matrix is an epoxy based resin hardened by an aliphatic polyamine [4]. The diffusion parameters (*cf.* Table 1) for both Fick and Langmuir models come from a minimization problem aiming at finding the optimal diffusion parameters in a least-square sense. We thus seek to minimize the distance between the experimental data available in [4] and the analytic solutions given in [2] for the Fick model and in [3] for the Langmuir model. In order to use those solutions, we assume that the diffusion is unidirectional within the matrix which is also considered as an homogeneous material at this scale. Figures 3(a) and 3(b) illustrate the absorption curves obtained with the identified parameters of each diffusion model. It can be seen on Figure 3(a) that the two models give very close results. Differences can however be observed on Figure 3(b) at the

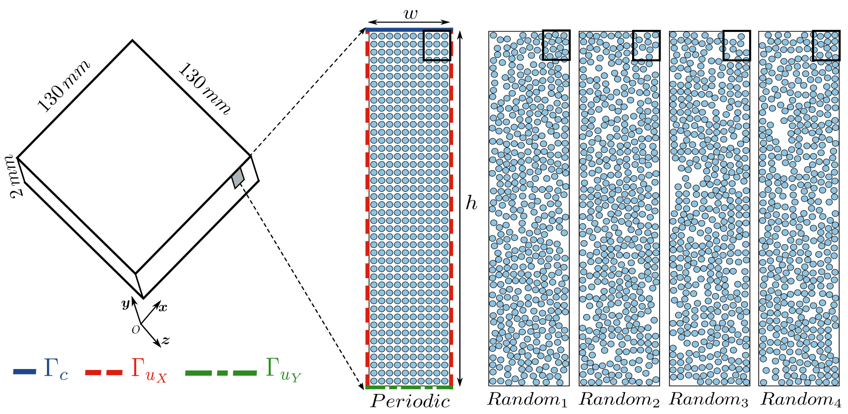


Figure 2. Geometry of microstructures (periodic and random) studied in this work, with boundary conditions for the diffusion and the mechanical problem.

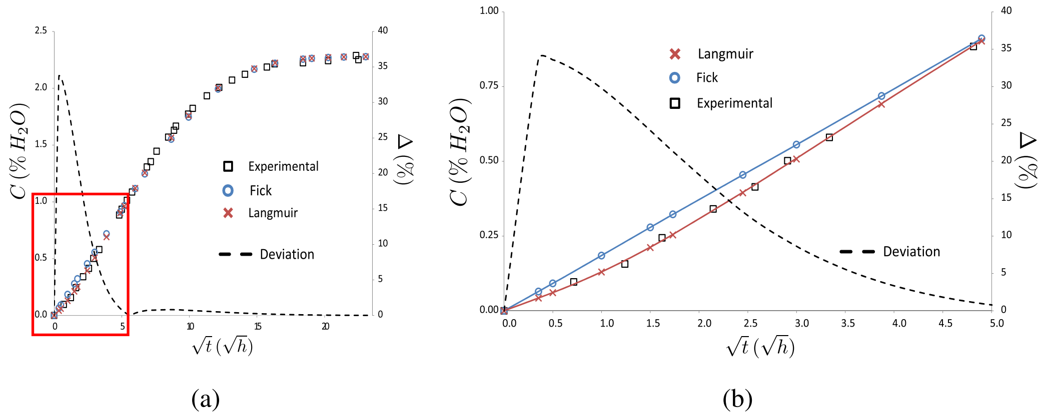


Figure 3. (a) Average water content $\bar{c}$ according to $\sqrt{t}$ in a pure resin sample: experimental data (squares), Fick identification (circles) and Langmuir identification (crosses). Δ (dotted line) is the relative deviation between Fick and Langmuir models. (b) Focus on the first instants.

very first instants of the diffusion process. According to the experimental data, the Fick model clearly overestimates the water content unlike the Langmuir model which better reproduces the diffusion in the beginning of the process. The hydrophobic reinforcements are made of glass. Table 1 presents the mechanical properties for each materials. E is the young modulus and ν is the Poisson's ration.

4.2. Geometries of microstructure

In this work, the water absorption by the edges may be neglected due to the samples dimensions: $130\,mm \times 130\,mm \times 2\,mm$. This lead to a symmetrical diffusion problem. For computational resources considerations, only a slice of the superior half of the sample is numerically represented where $h = 1.0\,mm$ and $w = 0.21\,mm$ (*cf.* Figure 2). Furthermore, the glass fibers are cylindrical with a fixed diameter of $18\,\mu m$. In order to be representative of naval applications, the mass fraction of reinforcement is close to 70 % inducing a volume fraction of $\nu_r \approx 53.3\,\%$. Five different geometries are considered: one periodic and four others obtained with the random generator described in section 3.2. The geometries of microstructure used in the numerical simulations are shown in Figure 2.

	Fick	Langmuir
$D\,(mm^2/s)$	1.47×10^{-6}	4.14×10^{-6}
$C^{\infty}\,(\%)$	2.28	2.28
$\alpha\,(s^{-1})$	X	8.76×10^{-5}
$\beta\,(s^{-1})$	X	5.34×10^{-5}

	Matrix	Reinforcements
$\rho\,(Kg/m^3)$	1220	2540
$E\,(MPa)$	2700	72500
ν	0.35	0.22
$\beta^h_x = \beta^h_y$	0.001	0.0

Table 1. Tables of diffusion parameters for each model and mechanical properties for each material.

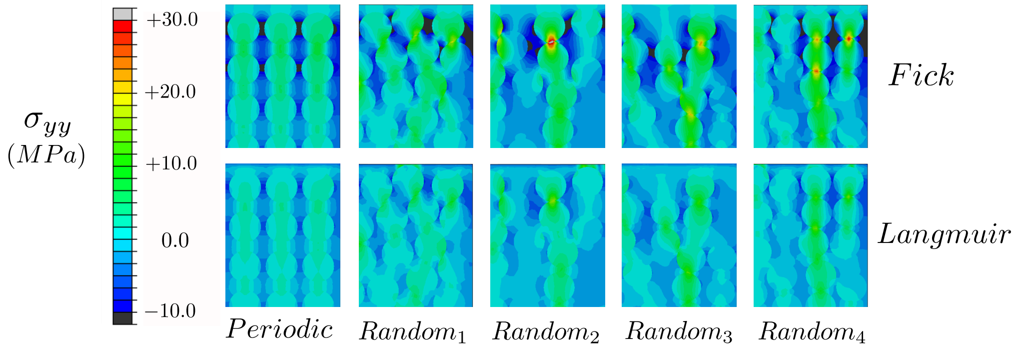


Figure 4. Stress fields σ_{yy} in the top right-hand corner of the five geometries obtained with Fick and Langmuir models at $t = 1\,h$.

4.3. Initial and boundary conditions

Samples are initially considered dry involving a zero moisture content within the matrix. The imposed moisture content c_{imp} applied on Γ_c is taken equal to the maximum moisture content C^{∞} (*cf.* Table 1). Symmetry conditions are used for the mechanical problem leading to decompose Γ_u into Γ_{u_X} (symmetry along X-axis) and Γ_{u_Y} (symmetry along Y-axis).

5. Results and Discussion

5.1. Local behavior

Figure 4 illustrates the σ_{yy} stress fields in the top right-hand corner of each geometry (*cf.* Figure 2) at $t = 1\,h$ which is representative of the transient part of the diffusion process. For all geometries, the Fick model leads to higher predicted local stresses. Those differences are explained by the mismatch of moisture content fields obtained with Fick and Langmuir models. The local moisture content is indeed higher with the Fick model for two combined reasons. Firstly, all the water molecules participate to the diffusion process with this model. Secondly, the sorption curve identified with the Fick model leads to a faster diffusion in the matrix during the first instants (*cf.* Figure 3(b)). Besides, we also notice a geometrical influence on the stress fields. For instance, the difference between the maximum local stresses obtained with each model are enhanced when the fibers are randomly distributed (3 MPa for the periodic case and 18 MPa for the $Random_3$ case). Figure 5 presents the stress fields σ_{yy} when the steady state is reached for each geometry. The geometry clearly impacts the local stresses for which significant discrepancies can be observed. Since we only use an uncoupled hygro-elastic model, both diffusion models lead to the same moisture contents and stationary stresses fields. However, adding a

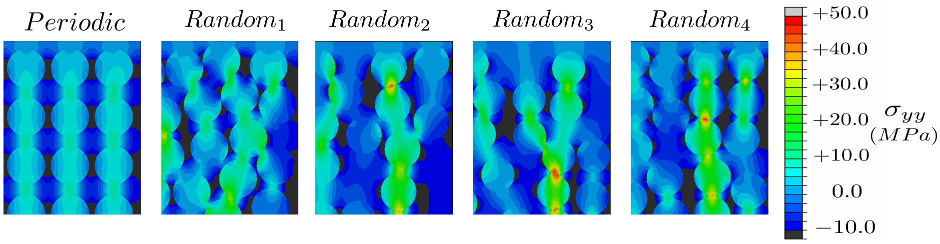
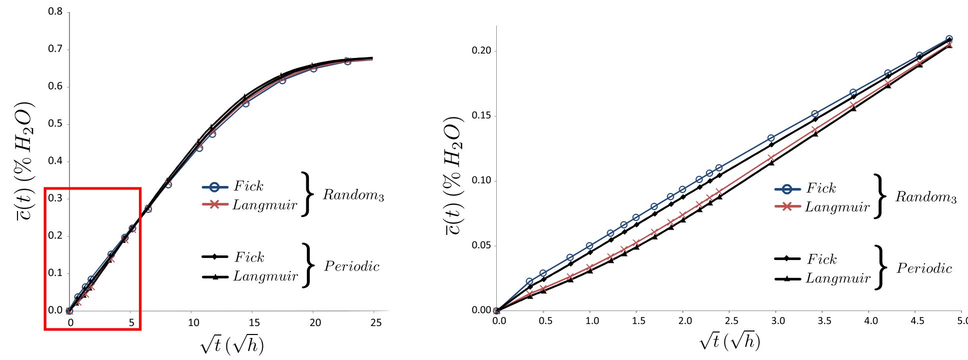


Figure 5. Stress fields σ_{yy} in the top right-hand corner of the five configurations at steady state.

coupling between the diffusion and mechanical models [5] and/or a local mechanical model, such as a damage model [6], could affect this observation. Further works will be devoted to the investigation of such local couplings.

5.2. Global behavior



(a) (b)

Figure 6. (a) Average water content $\overline{c}(t)$ with respect to $\sqrt{t}$ according to either Fick and Langmuir diffusion models and for *Periodic* and *Random*$_3$ configurations. (b) Highlight on the first instants.

We now focus on spatial average quantities. Figure 6 shows the evolution of the average content $\overline{c}(t)$ obtained with both models and for two geometries: *Periodic* and *Random*$_3$. We can observe that both models conduct to very close results. Only small differences comparable to the ones observed for the matrix diffusion behavior, *cf.* figure 3, appear. Moreover, changes in the geometry have small effects on the evolution of the average moisture content. We finally analyze

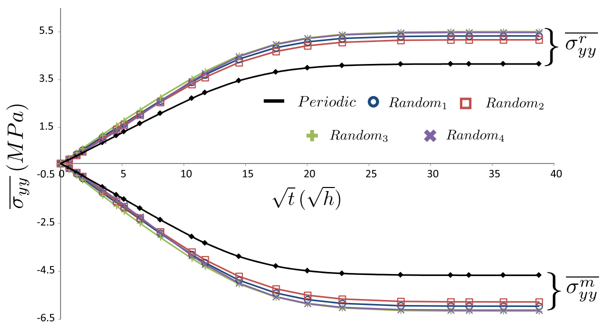


Figure 7. Mean stress inside the matrix $\overline{\sigma^m_{yy}}$ and the reinforcements $\overline{\sigma^r_{yy}}$ with respect of $\sqrt{t}$ for the five geometries.

the spatial average stress within the matrix and the reinforcements respectively denoted by $\overline{\sigma_{yy}^{m}}$ and $\overline{\sigma_{yy}^{r}}$. Figure 7 thus presents the evolution of $\overline{\sigma_{yy}^{m}}$ and $\overline{\sigma_{yy}^{r}}$ according to $\sqrt{t}$ for each geometries. For the sake of clarity, only results obtained from the Fick model are plotted since the Langmuir model gives close results. Firstly, it is worth noting that the matrix phase is in a global compression state when the fibers are in a global traction state. Secondly, it is important to highlight the deviation between the different geometries. In particular, the *Periodic* case presents a maximum relative deviation of 30 % corresponding to a gap of $\approx 1.5\,MPa$. This indicates that a more precise analysis of the effect of the distribution of the fibers is needed.

6. Conclusion

We have proposed a transient uncoupled hygro-elastic analysis of a polymer resin reinforced with hydrophobic glass fibers. The Fick and Langmuir diffusion models have been compared through numerical simulations. Using a dedicated random generator, effects of the geometrical distribution of the fibers have also been discussed. Analyses on both local and global quantities have shown discrepancies between the two models during the transient part of the moisture diffusion process whereas only the geometry affects the steady state results. Further works will be devoted to *(i)* analyze diffusion-mechanical couplings and *(ii)* use scale transition methods to take into account microscopic details at a much higher scale.

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 structure and super-structure), for their financial support.

References

[1] H. Ramezani Dana, A. Perronnet, S. Fréour, P. Casari, F. Jacquemin, Identification of moisture diffusion parameters in organic matrix composites, Journal of Composite Materials 47 (2013) 1081–1092.

[2] J. Crank, The mathematics of diffusion, 2^nd Edition, Oxford University Press, 1975.

[3] H. Carter, K. Kibler, Langmuir-type model for anomalous moisture diffusion in composite resins, Journal of Composite Materials 12 (1978) 118–131.

[4] Y. Joliff, L. Belec, M. Heman, J. Chailan, Experimental, analytical and numerical study of water diffusion in unidirectional composite materials - interphase impact, Computational Materials Science 64 (2012) 141–145.

[5] B. Eang-Sar, S. Fréour, P. Davies, F. Jacquemin, Coupling moisture diffusion and internal mechanical states in polymers: A thermodynamical approach, European Journal of Mechanics A/Solids 50 (2013) 541–550.

[6] A. Abhilash, S. P.Joshi, A. Mukherjee, L. Mishnaevsky Jr., Michromechanics of diffusion-induced damage evolution in reinforced polymers, CompSciTech 71 (2010) 333–342.