

# COUPLING MOISTURE DIFFUSION AND INTERNAL MECHANICAL STATES IN POLYMERS AND COMPOSITES – A THERMODYNAMICAL APPROACH

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## Abstract

We use a thermodynamical approach, based on the definition of the chemical potential of water, in order to establish a model coupling the diffusion of moisture to the mechanical states experienced by a polymer. The model enables to take into account the evolution, occurring during the diffusion process, of both the density of the polymer and its maximum moisture absorption capacity. The approach can be applied to the cases of an asymmetric loading in terms of relative humidity and external pressure. The model, established in the present work, provides the water content profiles in the thickness of the polymer throughout the transient phase of the diffusion process. The obtained numerical results show the significant effect, induced by the application of an external pressure on the kinetics of moisture diffusion in polymers.

**Keywords:** *Hygromechanical coupling, moisture absorption, thermodynamical approach.*

## 1. Introduction

Fiber reinforced organic matrix composites are being increasingly used for, as an example, aircraft, marine and civil engineering structural applications. Such composite structures are often submitted to humid environments during their service life [1]. Organic matrix composites do absorb significant amount of water when exposed to moisture. Many authors have reported that hygro-thermal ageing could induce a loss of the mechanical stiffness and/or strength of organic matrix composites [2]. Moreover, the constituents of composites structures exhibit heterogeneous coefficients of moisture expansion (CME) and maximum moisture absorption capacity. As a consequence, multi-scale in-depth mechanical states profiles rise during the hygroscopic loading of organic matrix composites. According to the literature, the resulting mechanical states can eventually induce damage [3-4]. Therefore, considerable efforts have been made by researchers in order to develop analytical models

enabling to predict the multi-scale mechanical states occurring during both the transient stage and the permanent regime of the moisture diffusion process of organic matrix composites submitted to hygro-mechanical loads [5-6]. In this field of research, the most recent investigations [7-9] focus upon taking into account, in the theoretical approaches, various features of hygro-mechanical coupling, observed during experimental studies, especially the dependence of both the moisture diffusion coefficient and the maximum moisture absorption capacity on the mechanical states (strains and stresses), [10-12]. These models aim eventually to enable the prediction of the long-term durability of composite structures submitted to hygroscopic loads. The purpose of this study is to establish a model coupling the diffusion of moisture to the mechanical states by a thermodynamical approach based on the expression satisfied by the chemical potential of water. The objective of the work is to extend the model proposed in [8] to the cases when the studied

structure is experiencing an unsymmetrical hygro-mechanical loading. Moreover, the present study aims to consider additional factors that have not yet been taken into account, such as the evolution of the polymer density as a function of the mechanical states, which occurs in practice during the moisture diffusion process.

## 2. Conservation of mass equation

The uncoupled law of Fick is classically used for modeling the diffusion of moisture in organic matrix composites. The adjective ‘‘uncoupled’’ refers to the fact that the model disregards any effect due to the mechanical states on the moisture diffusion process. The experimental investigation reported in [13] shows the anomalous transport of sorption process (i.e. it deviates from the Fickian transport). According to [14], the anomalies could be explained by coupled constitutive equations, based on the principles of continuum mechanics and irreversible thermodynamics.

In practice, the method relates the flux of moisture to the chemical potential  $\mu$ :

$$J_i = -\frac{DC}{RT} \nabla \mu \quad (1)$$

Where D is the diffusion coefficient in [mm<sup>2</sup>/s], C is the moisture content in [%], R is the perfect gases constant in [kJ/(mol.K)], T is temperature in [K].

The coupled diffusion equation which expresses the law of mass conservation is given by [15]:

$$\frac{\partial C}{\partial t} + J_{i,i} = 0 \quad (2)$$

## 3. Chemical potential

The chemical potential of water  $\widetilde{\mu}_e(C)$  is defined by the partial derivative of free energy of Helmholtz,  $F = F_0 + n_p f_e(C) + V_p$ , (where  $F_0$  is the free energy of the dry, stress-free polymer,  $f_e(C)$  is the variation of the free energy per mole of dry polymer, due to the addition of water when the polymer is free to swell,  $n_p$  and  $V_p$  are respectively the amount of polymer and its volume at actual state, whereas the amount of water is denoted by  $n_e$  [8]:

$$\widetilde{\mu}_e(C) = \frac{\partial F}{\partial n_e} = \frac{\partial F}{\partial C} \frac{\partial C}{\partial n_e} \quad (3)$$

The moisture content in the polymer is calculated through  $C = \frac{n_e \omega_e}{n_p \omega_p}$ , where  $\omega_e, \omega_p$  stand respectively for the molar mass of water and polymer.

The hygro-elastic strain energy is defined by:

$W = \frac{1}{2} \boldsymbol{\sigma} : \boldsymbol{\epsilon}^{el} = \frac{k}{2} (tr \boldsymbol{\epsilon} - 3\eta C)^2 + G \boldsymbol{e} : \boldsymbol{e}$ , where  $k$  and  $G$  are the bulk and shear modulus, respectively,  $\boldsymbol{\epsilon}^{el}$  is the elastic strain,  $\boldsymbol{\epsilon}$  is the total strain,  $\boldsymbol{e}$  is deviatoric strain tensor, and  $\eta$  is the coefficient of moisture expansion.

The chemical potential can finally be written as:

$$\widetilde{\mu}_e(C) = \frac{\omega_e}{\omega_p} f_e'(C) + \frac{\omega_e}{\rho_p} \left\{ \frac{k'(C)}{2} (tr \boldsymbol{\epsilon} - 3\eta C)^2 + G'(C) \boldsymbol{e} : \boldsymbol{e} \right\} + k(tr \boldsymbol{\epsilon} - 3\eta C) (-3\eta) \frac{\omega_e}{\rho_p} \quad (4)$$

Where  $\frac{\omega_e}{\omega_p} f_e'(C) = \mu_0 + RT \ln \frac{C}{C_0}$ ,  $\mu_0$  denoting the chemical potential of water in the strain-free polymer, whereas the reference moisture content is given by  $C_0$ .

During the moisture diffusion process, we take into account the evolution of the volume occupied by the polymer, and the resulting variation of its density :

$$\frac{V_p}{V_0} = \frac{\rho_0}{\rho_p} = tr \boldsymbol{\epsilon} + 1 \quad (5)$$

Where  $V, \rho$  stand respectively for the polymer volume and its density. The indices (p, 0) denote the present and initial state.

Assuming the mechanical properties of the polymer independent from the both the mechanical states and the moisture content, the chemical potential writes:

$$\widetilde{\mu}_e(C, tr \boldsymbol{\epsilon}) = \mu_0 + RT \ln \frac{C}{C_0} - \frac{3\eta \omega_e k}{\rho_0} (tr \boldsymbol{\epsilon} - 3\eta C)(tr \boldsymbol{\epsilon} + 1) \quad (6)$$

## 4. Hygroscopic pressure

The hygro-elastic Hooke’s law reads:

$$\epsilon_{ij} = \frac{1+\nu_p}{E_p} \sigma_{ij} - \frac{\nu_p}{E_p} (tr \sigma_{ij}) \delta_{ij} + \eta C \delta_{ij} \quad (7)$$

Where the term  $\eta C \delta_{ij}$  is the deformation of swelling,  $\nu_p$  is Poisson’s ratio,  $E_p$  is Young’s modulus, and  $\delta_{ij}$  is the Kronecker delta.

The total pressure  $P$  load results from the sum of the external pressure  $P_{ex}$  and the hygroscopic internal pressure  $P_{is}$  is triaxial,  $P = P_{ex} + P_{is}$ :

$$\sigma_{ij} = \begin{pmatrix} -P & 0 & 0 \\ 0 & -P & 0 \\ 0 & 0 & -P \end{pmatrix} \quad (8)$$

The Beltrami-Michell equation leads to:

$$(1 + \nu_p)\sigma_{ij,kk} + \sigma_{kk,ij} + E_p\eta \left( \frac{1+\nu_p}{1-\nu_p} \delta_{ij}C_{,kk} + C_{,ij} \right) = 0 \quad (9)$$

Furthermore, we get:

$$\Delta \left( tr\sigma_{ij} + 2\eta \frac{E_p}{1-\nu_p} C \right) = 0 \quad (10)$$

As a consequence, the hygroscopic pressure depends on the moisture content through:

$$\Delta P_{is} = \frac{\alpha}{A_0} \eta \Delta C \quad (11)$$

Where  $\frac{\alpha}{A_0} = \frac{2E_p}{3(1-\nu_p)}$  and  $A_0 = \frac{3\omega}{RT\rho_0}$ .

The solution of equation (11) satisfies:

$$P_{is}(x, t) = \frac{\alpha}{A} \eta C(x, t) + k_1(t)x + k_2(t) \quad (12)$$

The constants  $k_1(t)$  and  $k_2(t)$  are deduced from the following boundary conditions in which  $e$  is the plate thickness:

$$\int_0^e P_{is}(x, t) dx = 0 \quad (13)$$

$$\int_0^e P_{is}(x, t)x dx = 0 \quad (14)$$

The final form of equation (12) is given by:

$$P_{is}(x, t) = \frac{\alpha}{A} \eta (C(x, t) - 4\overline{C}(t)) + \frac{6}{e^3} \frac{\alpha}{A} \eta x (e^2 \overline{C}(t) - 2I) + \frac{6}{e^2} \frac{\alpha}{A} \eta I \quad (15)$$

Where

$$\overline{C}(t) = \frac{1}{e} \int_0^e C(x, t) dx, \quad I = \int_0^e xC(x, t) dx$$

## 5. Equation of model

The constitutive equation is obtained by using the mass conservation equation (2) in which the chemical potential of water has been written as a function of the trace of the strains and the moisture content:

$$\frac{\partial C}{\partial t} = \frac{D}{RT} \operatorname{div} \left[ C \left( \overrightarrow{\operatorname{grad}} \tilde{\mu}_e(C, tr\epsilon) \right) \right] \quad (16)$$

By considering the chemical potential  $\tilde{\mu}_e(C, tr\epsilon)$ , the model's equation reads:

$$\begin{aligned} \frac{\partial C}{\partial t} = & D \left[ \Delta C + \frac{9\eta^2 k \omega_e}{RT\rho_0} C (tr\epsilon + 1) \Delta C + \right. \\ & \left. \frac{9\eta^2 k \omega_e}{RT\rho_0} \overrightarrow{\operatorname{grad}} [C (tr\epsilon + 1)] \overrightarrow{\operatorname{grad}} C - \frac{3k\omega_e \eta}{RT\rho_0} (2tr\epsilon - \right. \\ & \left. 3\eta C + 1) C \Delta tr\epsilon - \frac{3k\omega_e \eta}{RT\rho_0} \overrightarrow{\operatorname{grad}} [(2tr\epsilon - 3\eta C + \right. \\ & \left. 1) C] \overrightarrow{\operatorname{grad}} tr\epsilon \right] \quad (17) \end{aligned}$$

Finally, the model can be applied to unsymmetrical loading in terms of moisture and/or pressure:

$$\begin{aligned} \frac{\partial C}{\partial t} = D \left[ (1 + V_1 \eta^2 C + V_2 \eta^3 C^2) \frac{\partial^2 C}{\partial x^2} + \eta^2 (V_3 + \right. \\ \left. V_4 C) \left( \frac{\partial C}{\partial x} \right)^2 + \right. \\ \left. \left( \frac{P_2 - P_1}{e} (V_5 + V_6 \eta^2 C) - \frac{6}{e^3} \frac{\alpha}{A} \eta (e^2 \overline{C}(t) - 2I) (V_5 + \right. \right. \\ \left. \left. V_6 \eta^2 C) \right) \frac{\partial C}{\partial x} - \frac{2A_0 \eta C}{k} \left( \frac{P_2 - P_1}{e} \right)^2 - \alpha \eta^2 C \frac{24}{k e^3} (e^2 \overline{C}(t) - \right. \\ \left. 2I) \frac{P_2 - P_1}{e} - \frac{72}{e^6} \frac{\alpha^2 \eta^3 (e^2 \overline{C}(t) - 2I)^2}{Ak} C \right] \quad (18) \end{aligned}$$

Where  $V_1 = -3A_0 k C tr\epsilon + 2\alpha tr\epsilon + \alpha$ ;

$V_2 = 9A_0 k - 3\alpha$ ;  $V_3 = \alpha - 3A_0 k tr\epsilon + 2\alpha tr\epsilon$ ;

$V_4 = 9\eta A_0 k + 3\eta \alpha - \frac{2\eta \alpha^2}{A_0 k}$ ;  $V_5 = 2A_0 \eta tr\epsilon + A_0 \eta$  and

$V_6 = 3A - 4 \frac{\alpha}{k}$

## 6. Boundary condition

The boundary condition is obtained by equating the chemical potential of water in humid air,  $\hat{\mu}_e = \hat{\mu}_0 + RT \ln \frac{p_e}{p_0}$  (where  $\hat{\mu}_0$  is the chemical potential of water in humid air at the reference pressure  $p_0$ . The partial pressure of water being  $p_e$ ) with the generalized

chemical potential of the polymer. Henry's law is introduced to define sorption isotherm:  $C_s = S p_e$  where  $S$  is the solubility of water given by  $S = \frac{C_0}{p_0} e^{\frac{\hat{\mu}_0 - \mu_0}{RT}}$ . In the case of a symmetrical hygro-mechanical loading the boundary equation is:

$$C(0, t) = S p_e \frac{1 + \left(\frac{A}{\alpha} \eta P_{ex} - \eta^2 \overline{C}(t)\right) (3A P_{ex} - 3\alpha \eta \overline{C}(t) - \alpha)}{1 - (3A P_{ex} - 3\alpha \eta \overline{C}(t) - \alpha) \eta^2 S p_e}$$

Where the external pressure follows this condition:

$$0 \leq P_{ex} \leq \frac{\epsilon - \alpha \eta^2 (3\eta C + 1) [C(0, t) - \overline{C}(t)]}{A \eta (3\eta C + 1)}, \epsilon \rightarrow 0$$

## 7. Numerical Results

The numerical simulations corresponds to a 4 mm thick plate made of Epoxy resin whose Young modulus is 3.65GPa and Poisson's ratio 0.36.

### 7.1. Symmetrical pressure and humidity loading

Figure 1 shows the time-dependent evolution of the macroscopic (average) moisture content in the plate, as a function of the CME:  $\eta = 0$ ;  $\eta = 0.2$  or  $\eta = 0.5$ , at an imposed pressure of 5 MPa.

The increase of CME leads to reduce the maximum moisture absorption capacity of the polymer indicated by the evolution of the average moisture content in the steady state.

The evolution of the moisture content profiles in the thickness of the plate during the transient process of the diffusion is drawn on figure 2 in the case that a symmetrical pressure of 5MPa and  $\eta = 0.5$  are considered.

According to figure 2, the moisture content at the boundary with the ambient fluid significantly varies throughout the transient regime. This means that the maximum moisture absorption capacity does not immediately reach its ultimate value. This effect comes from the dependence of the boundary condition on the mechanical strain experienced by the polymer, the magnitude of which considerably changes during the transient part of the diffusion process, due to the hygroscopic swelling. The obtained results are consistent with those published in reference [9].

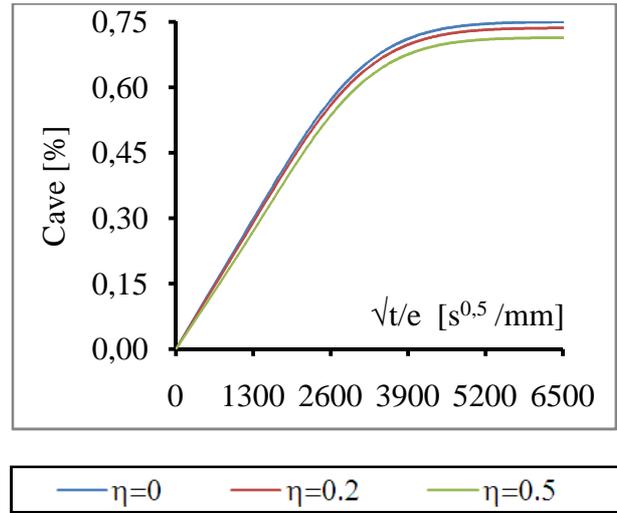


Fig. 1: Effect of CME on the average moisture content

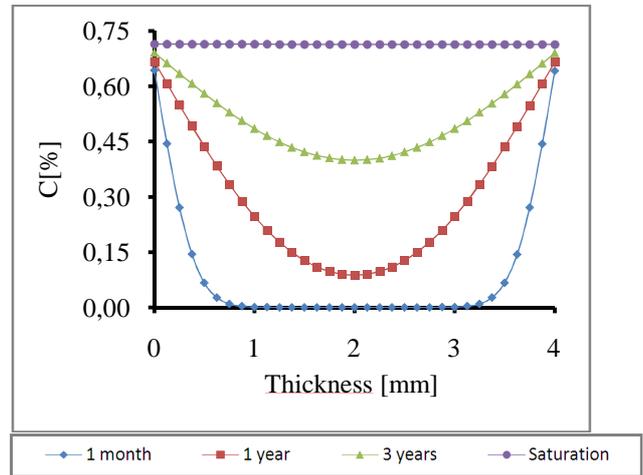


Fig. 2: In-depth time-dependent moisture content profiles

Figure 3 shows the effect induced by the application of an external pressure, varying from 1 MPa to 100 MPa, on the time-dependent moisture content, at the interface between the solid and the ambient fluid. According to figure 3, an increased applied pressure significantly reduces the diffusion of moisture at the boundary.

Figure 4 shows that the maximum moisture absorption capacity reached in the steady state depends almost linearly on the applied pressure. The results are consistent with [16].

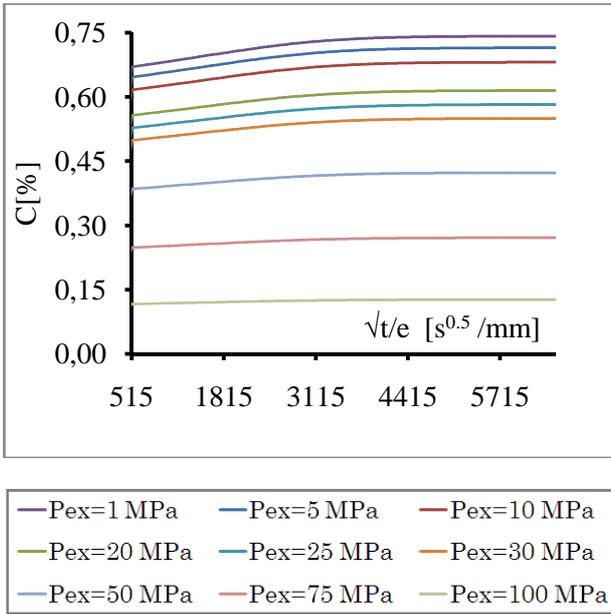


Fig. 3: Time-dependent moisture content at the boundary, as a function of the applied pressure.

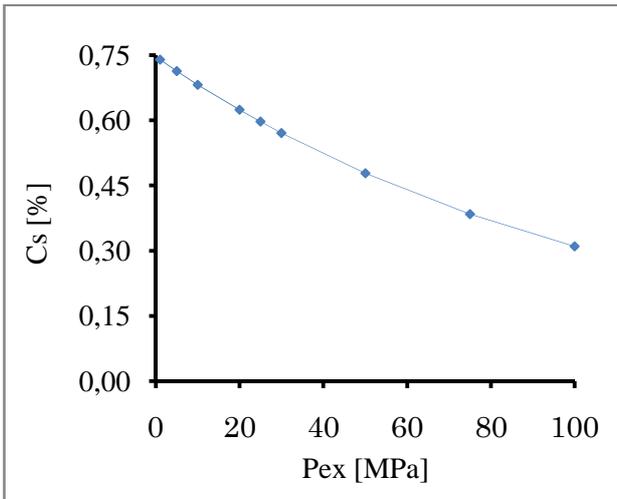


Fig. 4: Maximum moisture absorption capacity in steady state, as a function of the applied external load.

The results of the simulations show that the apparent coefficient of diffusion is almost independent from the applied external load (Figure 5).

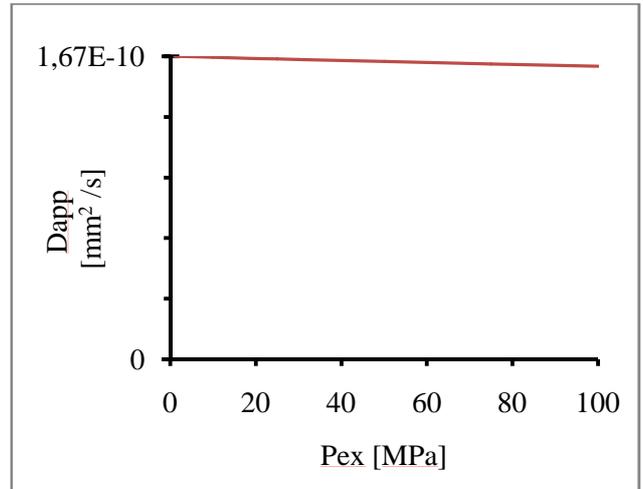


Fig. 5: Apparent moisture diffusion coefficient, as a function of the applied external load

## 7.2. Asymmetrical applied pressure

In the case when the pressure applied to the right side of the plate is higher than its left counterpart ( $P_1 = 1$  MPa,  $P_2 = 10$  MPa,  $\eta=0.5$ , the hygroscopic loading being symmetric), the right side absorbs less moisture than the left side. The unsymmetrical moisture content profiles in the plate shown on figure 6 result from the pressure gradient.

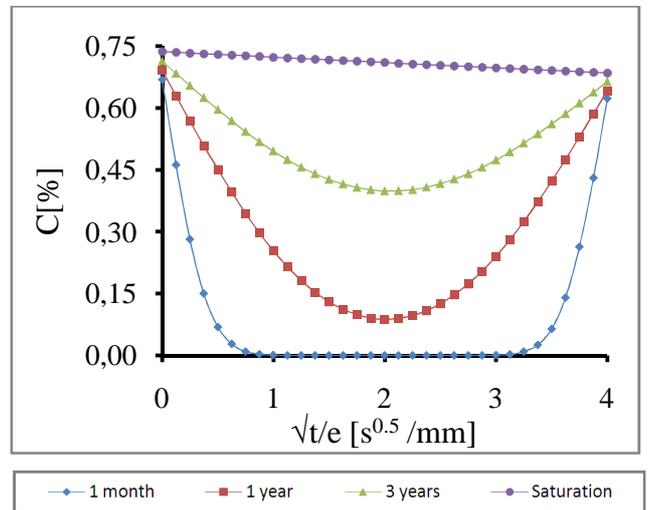


Fig. 6: Moisture diffusion under an asymmetric external pressure.

## 8. Conclusion

The present work is dedicated to the establishment of a model enabling to predict the moisture diffusion within polymers under external load (pressure). The

moisture sorption results from coupled hygro-mechanical phenomena. The developed model is a first enrichment compared to many previous works based on empirical approaches such as a the free-volume theory. By comparison to the works based on the thermodynamical approach, such as [8] the present model accounts the dependence of the polymer density on the mechanical states, which was previously neglected. Moreover, the present study extends the thermodynamical approach to the cases of an asymmetrical loading in terms of either (or both) the hygroscopic or the mechanical loads. The simulations reproduce the expected evolutions, as a function of the applied external pressure, of the maximum moisture absorption capacity. These results are compatible with the experimental investigations [17]. On the contrary, the apparent diffusion coefficient predicted by the model is almost independent from the pressure load. That is actually incompatible with the practical observations reported in the literature. As a consequence, improvements should be achieved in further investigations. In future work, realistic evolutions of the hygro-mechanical properties (i.e. the elastic moduli and coefficient of moisture expansion), occurring during the diffusion process, will be taken into account. Finally, the model presented in this communication will be extended to the case of polymer matrix composites.

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