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Water–Mechanical Property Coupling

F. Jacquemin and S. Fréour

Abstract The present contribution investigates the effects related to the plasticization of the polymer matrix occurring during the water sorption process on the internal mechanical state profiles, at the constituent and ply scales. Then, two multi-physics models are considered to account that the moisture sorption depends on the internal mechanical states: the free volume theory and a thermodynamic approach.

1 Introduction

A Fickian diffusion, governed by the maximum absorption capacity and the diffusion coefficient, is often considered to model the moisture sorption process occurring in composite materials subjected to ambient relative humidity. Moisture sorption can lead to a plasticization of the constitutive organic resin. This entails a decrease of some mechanical properties such as the Young modulus. This phenomenon, referred to as “*weak coupling*”, as only the mechanical properties are moisture dependent, will be investigated first. The aim is to account for plasticization effects in the predictive models dedicated to the determination of the multi-scale internal mechanical states (at the ply scale and in the constituents of the ply) during the moisture diffusion process. If the moisture sorption presents a more complex behavior, more elaborated approaches can be used. In that context, instead of Fick’s model, one can use Langmuir’s model or “*strong*” stress-

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diffusion coupling models such as the free volume theory or thermodynamically based model. The so-called “*strong coupling*” models enable the fact that the moisture sorption is dependent on the mechanical states and vice versa, to be taken into account. In this work, two coupling models are considered: a phenomenological approach based on the free volume concept, and a more fundamental model, based on a thermodynamic approach.

2 Plasticization Effects on the Multi-Scale Internal Stresses

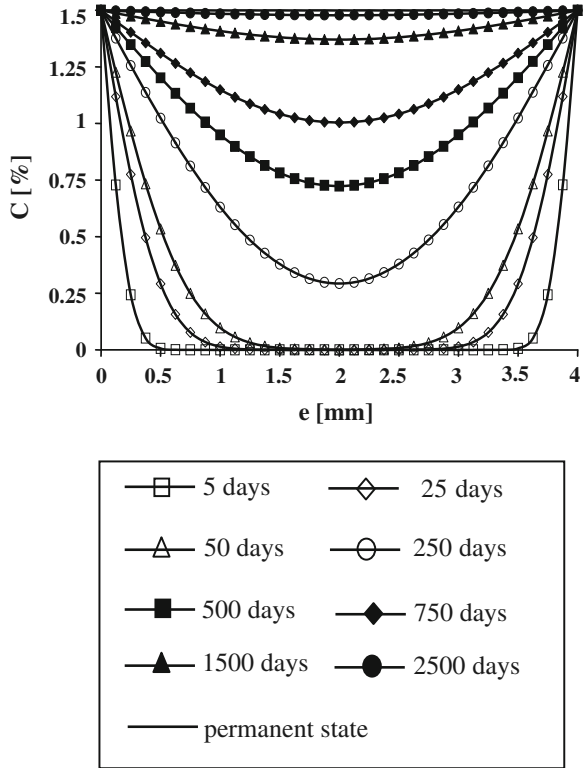
This work investigates the plasticization effects related to the evolution, as a function of the moisture content, of the hygro-elastic properties on the internal stress states during the transient part of a hygroscopic load. The proposed approach involves the coupling of the classical continuum mechanics formalism presented by Jacquemin and Vautrin [5] to Eshelby-Kröner self-consistent scale transition model recently extended to account for a hygroelastic load [4, 6, 7]. An inverse scale transition model provides, from the experimental macroscopic ply moduli (Table 1), the evolution of the local hygro-elastic properties experienced by the epoxy matrix as the moisture diffusion takes place. Figure 1 shows the moisture diffusion process inside a composite structure following a Fickian behavior. According to Fig. 2, the fact of considering the plasticization and thus an evolution of the hygro-elastic properties of both the composite plies and its constitutive matrix strongly affects the transverse stresses levels and their distributions in the plies and their constituents.

Figure 2 depicts the classical results expected in the case where a unidirectional composite is subjected to a transient hygroscopic load: the high macroscopic stresses arising at the beginning of moisture diffusion thereafter decrease and disappear as soon as the permanent state is reached. However, the absolute values of the corresponding transverse stresses at the constituent scale increase almost uninterruptedly during the moisture diffusion process, reaching their maximum when the saturation state is attained. It should be emphasized that, in this specific case, the transverse stress calculated for the carbon fiber varies significantly, depending on the choice of the hypothesis for the relationship between material properties and moisture content.

Table 1 Experimental macroscopic elastic moduli as a function of the moisture content [9]

Moisture content ΔC^I (%)	0	0.25	0.75
E_1^I (GPa)	130	130	130
E_2^I (GPa)	9.5	9.25	8.75
ν_{12}^I	0.3	0.3	0.3
G_{12}^I (GPa)	6.0	6.0	6.0
G_{23}^I (GPa)	3.0	3.0	3.0

Fig. 1 Time and space dependent moisture content profiles in the composite structure



According to the foresaid, taking account of changes in the multiscale hygroelastic properties of composite plies when the matrix experiences plasticization has two main consequences, that can be considered responsible for the reduced estimated stresses compared with their reference values (calculated disregarding the effect of moisture on material properties). First, sharp distinctions occur between the effective properties of the wet materials and their counterparts in the dry composite. This effect increases with time, as the amount of water in the structure grows, and reaches its maximum when the permanent stage of the diffusion process is attained.

Since the predicted stresses are obviously intimately linked to the hygroelastic properties of the material, this effect partially explains the discrepancies between the two sets of curves displayed in Fig. 2. Second, gradients of moisture content arise in the composite during the transient stage of moisture diffusion in it, since the process is rather slow (see Fig. 1). The distribution of the hygroscopic load within the thickness of the structure directly induces a distribution of the hygroelastic properties of materials if their dependence on moisture content is taken into account in calculations. The non uniform distribution of hygromechanical properties explains the distinctions occurring at the beginning of the moisture diffusion process, between the internal stresses predicted with and without taking account of

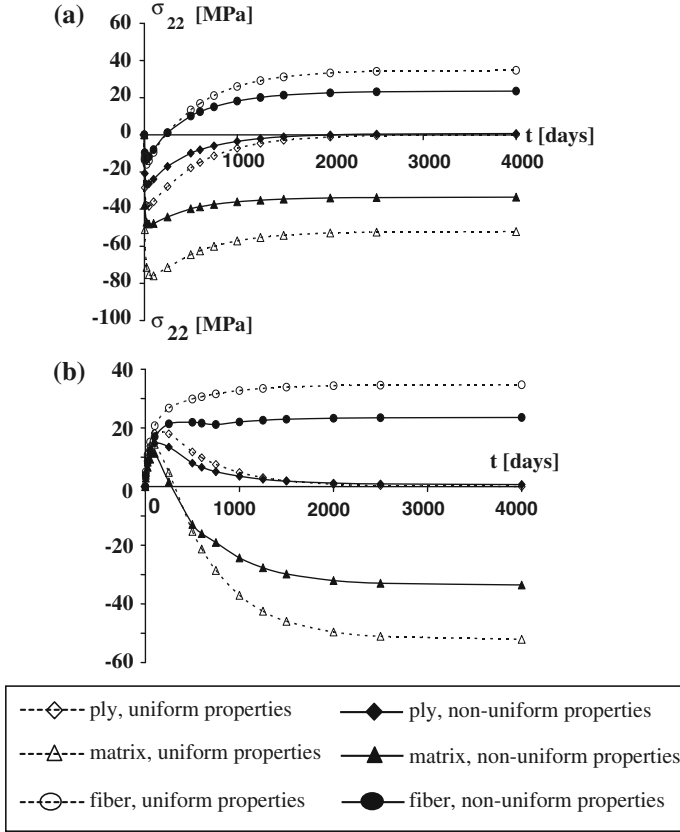


Fig. 2 Effect of the plasticization on the multi-scale stress states in (a) the external ply (b) the central ply of a uni-directional composite during the transient part of the moisture diffusion process

the effect of moisture on material properties. Thus, increased internal stresses, related to softening of the material induced by the diffusion of water, can be expected even at the beginning of hygroscopic loading of a composite structure.

3 The Free Volume Theory

Historically, a theoretical approach based on the calculation of the free-volume change in the stressed state was developed by Neumann and Marom [8]. Assuming that the Fickian diffusion coefficient was related to the free volume by the Doolittle equation, Neumann and Marom [8] proposed an expression for the ratio of the diffusion coefficients in the strained and free-of-strain states:

$$\text{Ln} \left(\frac{D_\varepsilon^m}{D_0^m} \right) = \frac{a}{v^m} \left(\frac{1}{v_{f0}^m} - \frac{1}{v_{f\varepsilon}^m} \right) \quad (1)$$

where D_0^m and D_ε^m are the Fickian moisture diffusion coefficients for the strain-free matrix and that of the strained epoxy, respectively, where a is an empirical factor. v^m denotes the volume fraction of the matrix in the composite ply, v_{f0}^m and $v_{f\varepsilon}^m$ are the free volume fraction of the strain-free and strained epoxy matrix, respectively. These quantities are related by the trace of the strain tensor $\text{Tr } \varepsilon^m$ through:

$$v_{f\varepsilon}^m = v_{f0}^m + \text{Tr } \varepsilon^m \quad (2)$$

The maximum moisture absorption capacities for an unstrained matrix and a strained matrix are related through the following equation:

$$M_{\infty\varepsilon}^m = M_{\infty 0}^m + (v_{f\varepsilon}^m - v_{f0}^m) \times \frac{\rho^w}{\rho^m} = M_{\infty 0}^m + \text{Tr } \varepsilon^m \times \frac{\rho^w}{\rho^m} \quad (3)$$

where ρ^w and ρ^m are respectively the densities of water and resin.

The macroscopic moisture content is assumed to be the solution of Fick's equation with a moisture diffusion coefficient dependent on the local mechanical state, as presented by Youssef et al. [14]. A scale transition approach provides relations linking the ply stresses (strains) to those of the constituents, as well as homogenization procedures enabling the evolution of the plies diffusive behaviour throughout the transient part of the diffusion process to be estimated.

According to Fig. 3, the coupled hygro-mechanical model leads to a maximum moisture absorption capacity of 1.5 % in the unidirectional structure and 1.37 % only in the case of the $\pm 55^\circ$ laminate. This is actually due to a discrepancy between the mechanical strain states experienced by the two considered structures.

Figure 4 shows the transverse stresses evolution in the internal ply of (a) the laminated (b) the unidirectional cylinders, during the transient part of the diffusion.

According to Fig. 4, whatever the considered stacking sequences, the most significant discrepancies between the transverse stresses predicted by the coupled/uncoupled models occur at the beginning of the diffusion process. However, the discrepancy rapidly fades and cancels when the permanent state is attained in this structure. On the contrary, in the laminate, an absolute deviation of 10 MPa still holds in the permanent state of the diffusion process, regarding the predicted transverse stress experienced by the organic matrix.

4 The Thermodynamical Approach

Some experimental data demonstrate that the moisture sorption that takes place in composites structures could differ from the typical Fickian uptake (Cai and Weitsman [1, 10]). As a consequence, some researchers have developed models in order to

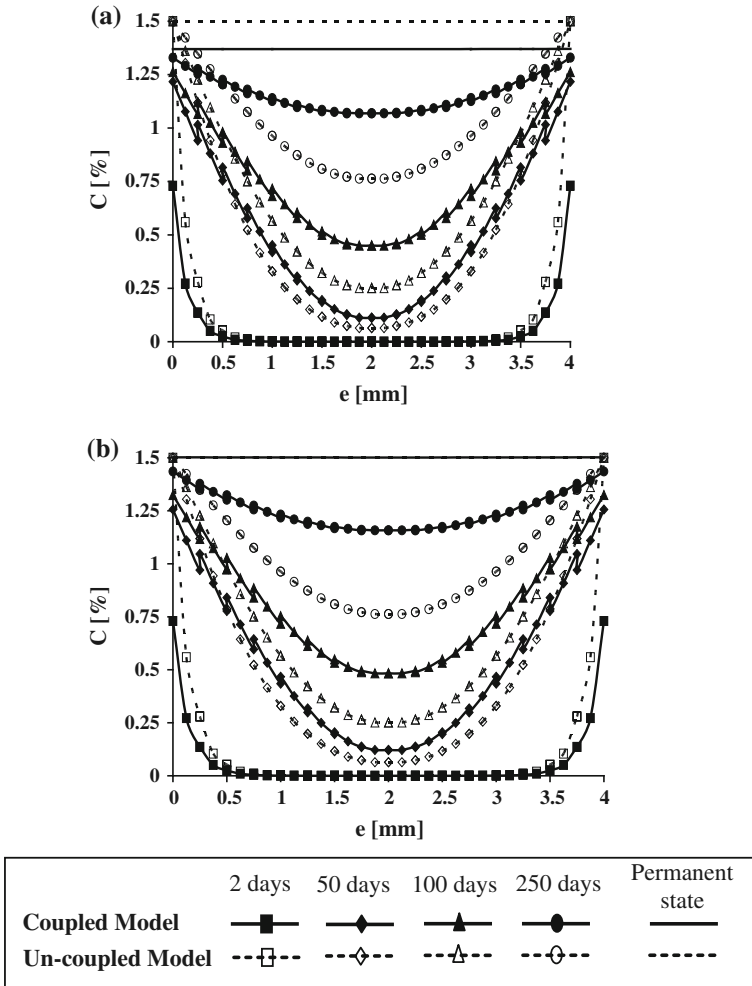


Fig. 3 Effect of a multiphysics approach on the predicted time and space dependent moisture content profiles in the (a) $\pm 55^\circ$ composite structure (b) unidirectional composite structure

reproduce the anomalous sorption curves observed in practice [2, 13]. Among the proposed methods, [11] documented a multi-physics approach to the diffusion mechanisms compatible with the thermodynamics. Recently [3, 12] published a model focused on the description of anomalous diffusion also developed upon the concept of being compatible with the thermodynamics.

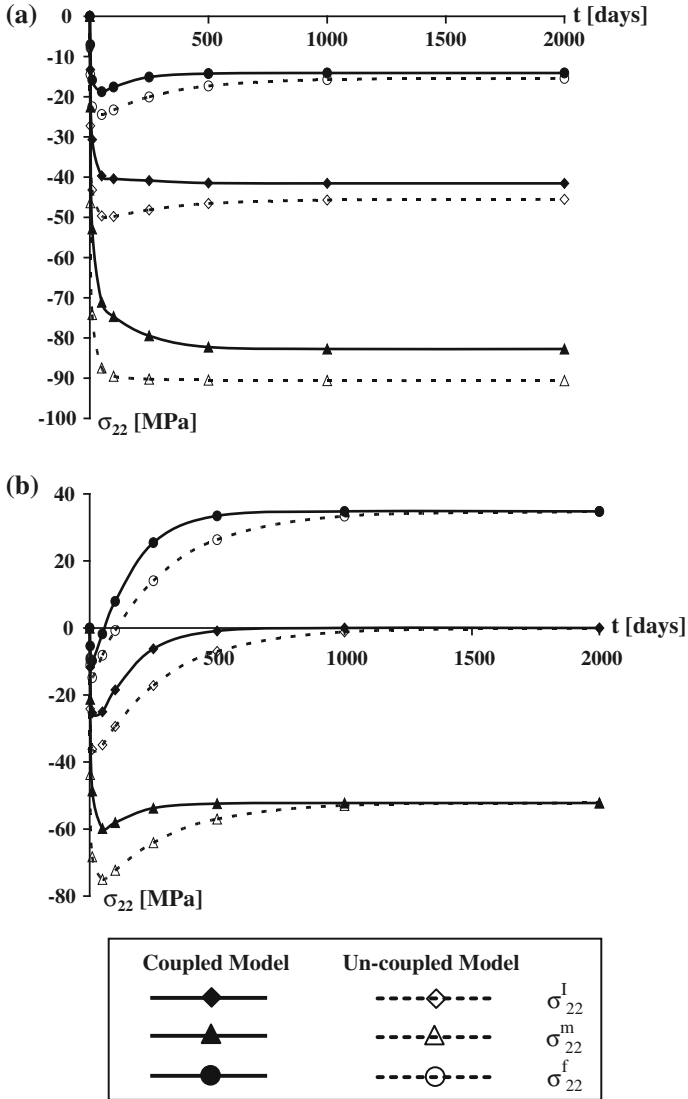


Fig. 4 Multi-scale transverse stress states in the internal ply of the **a** $\pm 55^\circ$ laminate **b** unidirectional composite structure

4.1 The Historical Model

The chemical potential $\tilde{\mu}_c$ is defined as the partial derivative of the free energy of Helmholtz F with respect to the amount of water n_w [3]:

$$\tilde{\mu}_w = \frac{\partial F}{\partial n_w} = \frac{\partial F}{\partial C} \frac{\partial C}{\partial n_w} \quad (4)$$

Starting from Eq. (4), one can express the moisture diffusion behavior law of a polymer. Let us first consider the mass density of the polymer to be constant throughout the moisture diffusion process. According to Derrien and Gilormini [3], in the case of a unidirectional diffusion in a polymer submitted to a hydrostatic load, the time dependent evolution of the moisture content respects:

$$\frac{\partial C}{\partial t} = \frac{D}{RT} \operatorname{div} \left[C \left(\overrightarrow{\operatorname{grad}} \tilde{\mu}_w \right) \right] = D \left[(1 + \alpha \eta^2 C) \frac{\partial^2 C}{\partial x^2} + \alpha \left(\frac{\partial C}{\partial x} \right)^2 \right] \quad (5)$$

$$\text{where } \alpha = \frac{2A_0 E_p}{3(1 - \nu_p)} \text{ and } A_0 = \frac{3\omega_w}{RT\rho_0}$$

D , E_p , ν_p , η and ρ_0 respectively denote the diffusion coefficient, Young's modulus, Poisson's ratio, coefficient of moisture expansion and the strain-free mass density of the polymer. ω_w stands for the molar mass of water.

4.2 Accounting for the Average Mass Density Experienced by the Polymer

The model described above assumes that the polymer mass density is independent from the strain state. This condition is actually not fulfilled in practice. The volume V_p of a strained polymer can be expressed as a function of both its strain-free counterpart V_0 and the trace of the strain tensor ε_p . As a consequence, the mass density ρ_p of a strained polymer can be written from the principle of matter conservation, as a function of ρ_0 :

$$\rho_p = \frac{m_p}{V_p} = \frac{m_0}{V_0} = \rho_0 \frac{1}{(\operatorname{Tr} \varepsilon_p + 1)} \quad (6)$$

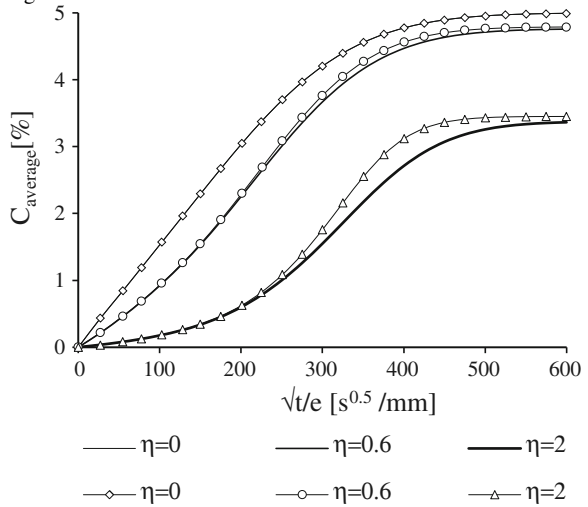
In the case that the evolution of the polymer average mass density during the diffusion process is accounted for, in the context of writing the moisture diffusion equation, one obtains [12]:

$$\frac{\partial C}{\partial t} = D \left[(1 + \alpha_1 \eta^2 C + \alpha_1 \eta^2 C^2) \frac{\partial^2 C}{\partial x^2} + \eta^2 (\alpha_3 + \alpha_4 C) \left(\frac{\partial C}{\partial x} \right)^2 \right] \quad (7)$$

where, $\alpha_1 = \operatorname{Tr}(\varepsilon_p)(2\alpha - 3A_0 k_p C) + \alpha$, $\alpha_2 = 3(A_0 k_p - \alpha)$, $\alpha_3 = \alpha + (2\alpha - 3A_0 k_p) \operatorname{Tr}(\varepsilon_p)$, $\alpha_4 = \eta \left[9A_0 k_p + \alpha \left(3 - \frac{2\alpha}{A_0 k_p} \right) \right]$.

Figure 5 shows the time-dependent evolution of the average moisture content, as a function of the Coefficient of Moisture Expansion.

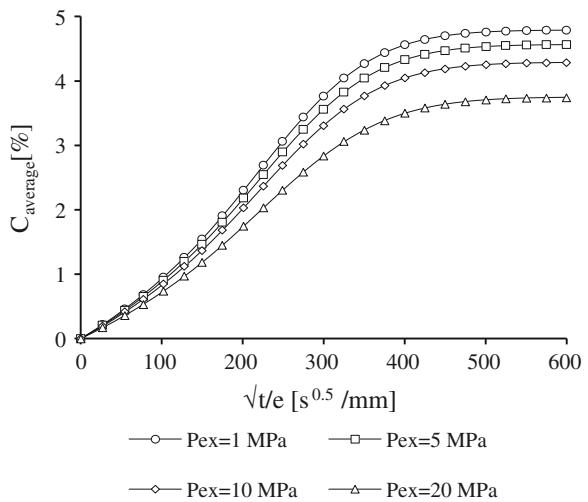
Fig. 5 Effect of CME on the average moisture content



According to Fig. 5, increasing CME reduces the maximum moisture absorption capacity of the polymer as indicated by the evolution of the average moisture content in the steady state. The continuous lines (without marks) show the results predicted by Derrien and Gilormini model, whereas the continuous lines with marks correspond to the model developed in the present work. The discrepancies between the models increase significantly with the coefficient of moisture expansion.

Figure 6 shows the effect induced by the application of an external pressure, varying from 1 to 20 MPa, on the time-dependent moisture content. The Coefficient of Moisture Expansion used in order to obtain the results depicted here is

Fig. 6 Effect of applied pressure on the average moisture content



equal to 0.6. Thus, the moisture absorption capacity of the polymer varies with the magnitude of the applied external pressure.

4.3 Accounting for the Hygroscopic Swelling

Moisture absorption induces swelling strains. The mathematical formalism presented in both references [3, 12] does not enable the effects induced by the presence of an in-depth heterogeneous profile of the hygro-elastic strain on the moisture kinetics to be accounted for. Thus further developments were brought to the thermodynamic based moisture diffusion model in order to address this issue.

Swelling strains actually correspond to the existence of a hygroscopic pressure within the material. The in-depth, time-dependent hygroscopic pressure profile occurring during the transient stage of the diffusion process is determined according to three equations: (a) Hygro-elastic Hooke's law; (b) Equilibrium equations and (c) Compatibility equations.

For the case when unidirectional diffusion is assumed to occur, the internal hygroscopic pressure P_{is} induced by a possibly unsymmetrical hygroscopic load (i.e. the structure is submitted to heterogeneous boundary conditions in term of hygroscopic conditions) can be written as follows:

$$P_{is}(x, t) = \frac{\alpha}{A_0} \left[\eta \left(C(x, t) - 4\overline{C(t)} \right) + \frac{6}{L^3} \eta x \left(L^2 \overline{C(t)} - 2I \right) + \frac{6}{L^2} \eta I \right] \quad (8)$$

where L stands for the thickness of the sample, $\overline{C(t)}$ is the average moisture content in the sample, and I corresponds to the following integral:

$$I = \int_0^L C(x, t) x \, dx \quad (9)$$

For the case where a symmetrical hygroscopic load is applied on the boundaries of the structure, $C(x, t) = C(L - x, t)$. As a result, the integration I is equal to $\frac{L^2 \overline{C(t)}}{2}$.

Hence, the corresponding hygroscopic pressure is given by the simplified form:

$$P_{is}(x, t) = \frac{\alpha}{A_0} \eta \left(C(x, t) - \overline{C(t)} \right).$$

During the moisture diffusion process, both the average (macroscopic) change of the polymer mass density, as well as the local hygroscopic swelling are accounted for. The first condition corresponds to the modifications described in Sect. 4.2 above. The hygroscopic swelling yields an in-depth continuous evolution of the local volume of the polymer as a function of the moisture content. The following expression should then be introduced in the derivative of the free energy of Helmholtz by the moisture content featured by the fundamental relation of the model (4):

$$\frac{\partial V_\varepsilon}{\partial C} = \frac{\partial V_\varepsilon}{\partial \text{tr } \varepsilon} \frac{\partial \text{tr } \varepsilon}{\partial C} = V_0 \frac{\partial \text{tr } \varepsilon}{\partial C} = \frac{n \omega}{\rho_0} \frac{\partial \text{tr } \varepsilon}{\partial C} \quad (10)$$

The resulting time-dependent diffusive behavior for a polymer plate submitted to an unsymmetrical humid ambient load is given by:

$$\begin{aligned} \dot{C} = D & \left[(1 + V_1 \eta^2 C + V_2 \eta^3 C^2) \frac{\partial^2 C}{\partial x^2} + \eta^2 (V_3 + V_4 C) \left(\frac{\partial C}{\partial x} \right) \right. \\ & \left. - \frac{6}{L^3} \frac{\alpha}{A_0 k} \eta \left(L^2 \overline{C(t)} - 2I \right) (V_5 + V_6 \eta^2 C) \frac{\partial C}{\partial x} - \frac{72}{L^6} \frac{\alpha^2}{A_0 k} \eta^3 \left(L^2 \overline{C(t)} - 2I \right)^2 C \right] \\ & + g \end{aligned} \quad (11)$$

where

$$\begin{aligned} V_1 &= -3 A_0 k \text{tr } \varepsilon + 2\alpha \text{tr } \varepsilon + \alpha, & V_2 &= 9 A_0 k - 3\alpha, \\ V_3 &= -3 A_0 k \text{tr } \varepsilon + 2\alpha \text{tr } \varepsilon + \alpha, & V_4 &= \eta V_2 - \frac{2 \eta \alpha^2}{A_0 k}, \\ V_5 &= 2 \eta A_0 \text{tr } \varepsilon + A_0 \eta, & V_6 &= 3 A_0 - 4 \frac{\alpha}{k} \end{aligned}$$

Besides, the factor g could be written as follows:

$$g = D \xi \left[z_1 \frac{\partial^2 C}{\partial x^2} + z_2 \left(\frac{\partial C}{\partial x} \right)^2 + z_3 \frac{\partial C}{\partial x} + 3C \left\{ \frac{6}{L^3} \frac{\alpha}{A_0 k} \eta \left(L^2 \overline{C(t)} - 2I \right)^2 \right\} \right] \quad (12)$$

where

$$z_1 = -3\eta(2 \text{tr } \varepsilon - 3\eta C + 1)C + (3 \text{tr } \varepsilon - 6 \eta C + 1)C \frac{3 A_0 k - \alpha}{A_0 k} \eta \quad (13)$$

$$\begin{aligned} z_2 &= -3\eta(2 \text{tr } \varepsilon - 6 \eta C + 1) + (3 \text{tr } \varepsilon - 18 \eta C + 1) \frac{3 A_0 k - \alpha}{A_0 k} \eta \\ &+ 3C \left(\frac{3 A_0 k - \alpha}{A_0 k} \eta \right)^2 \end{aligned} \quad (14)$$

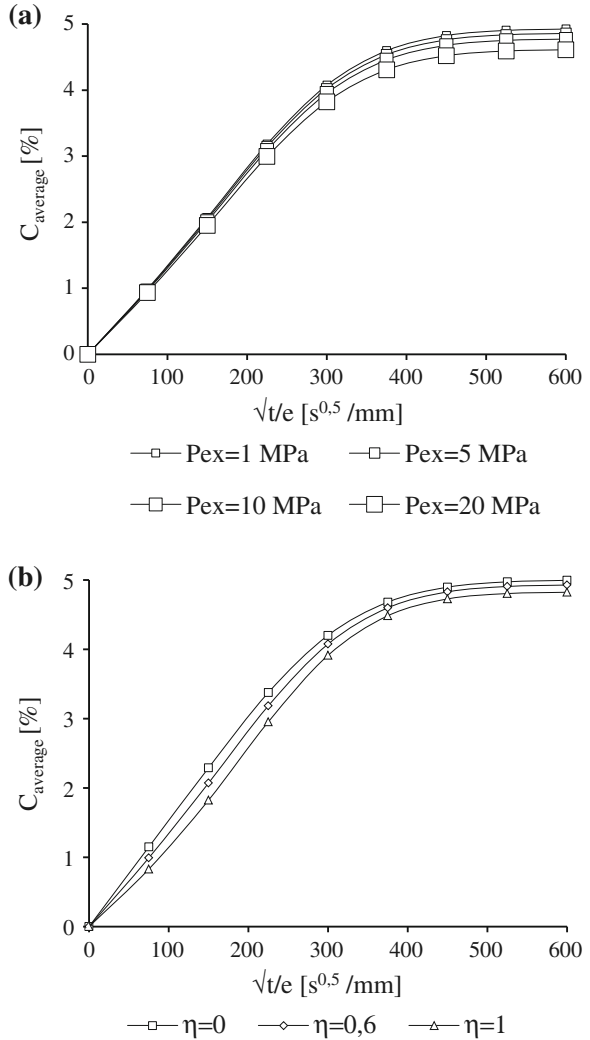
$$\begin{aligned} z_3 &= -\frac{6}{L^3} \frac{\alpha}{A_0 k} \eta \left(L^2 \overline{C(t)} - 2I \right) (3 \text{tr } \varepsilon - 18 \eta C + 1) \\ &- \frac{36 C}{L^3} \frac{\alpha}{A_0 k} \left(L^2 \overline{C(t)} - 2I \right) \frac{3 A_0 k - \alpha}{A_0 k} \eta^2 \end{aligned} \quad (15)$$

$$\xi = \frac{3 A_0 k - \alpha}{3} \eta \quad (16)$$

Figure 7 shows the time-dependent evolution of the average moisture content, as a function of the applied pressure and the coefficient of moisture expansion.

According to Fig. 7, increasing CME and pressure involve a reduction of the moisture absorption of the polymer as indicated by the evolution of the average

Fig. 7 a Effect of the applied pressure on the average moisture content ($\eta = 0,6$). **b** Effect of the moisture expansion coefficient on the average moisture content ($P_{ex} = 1 \text{ MPa}$)



moisture content. The maximum absorption capacity decreases with increasing the pressure and the CME. We retrieve a Fickian behaviour when the CME is equal to 0. This result does not depend on the applied pressure.

Figure 8a depicts the average moisture content in the case of an unsymmetrical loading: the moisture content on the external face can take a value of 0, 2.5 and 5 % (the moisture content on the other face is fixed at 5 %).

For unsymmetrical loading, the average moisture content does not vary linearly due to the coupling phenomenon. As expected, the average moisture content increases with the boundary moisture content.

Fig. 8 Effects of an unsymmetrical hygroscopic load on (a) the average moisture content ($\eta = 0.6$), (b) the moisture content profile (filled marks $\eta = 0$, marks not filled $\eta = 0.6$)

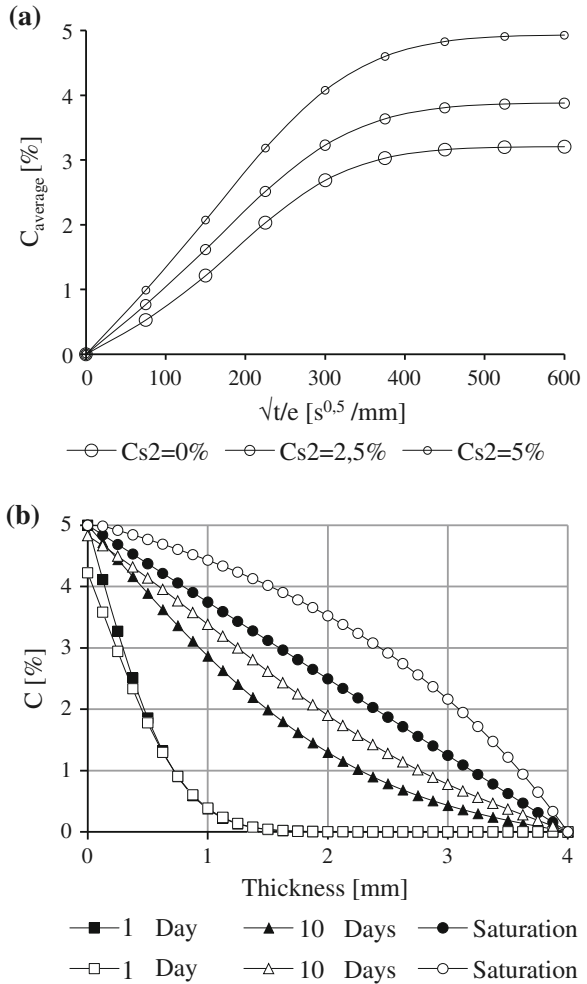


Figure 8b shows the moisture content profile when the boundary moisture contents on the internal and external faces are equal to 5 and 0 % respectively. We consider two different values for the CME: 0.6 and 0. For a CME of 0.6, the moisture content profile at saturation is not linear. A Fickian linear variation is observed when the CME is equal to 0. An unsymmetrical loading combined with a coefficient of moisture expansion different to 0 involves more important moisture contents. Thus, the effects induced by the through-thickness differential swelling on the time-dependent diffusion are pointed out.

5 Conclusions

The aim of the present work is to propose models enabling water-mechanical property coupling due to plasticization phenomenon or coupling between moisture diffusive behavior law and internal mechanical states to be taken into account, according to the free volume theory or the thermodynamic approach. For instance, the proposed development enables the effects induced by the presence of an in-depth heterogeneous profile of the hygro-elastic strain on the moisture kinetics to be accounted for. Such models can be used to represent several typical diffusive behaviors met experimentally. This field of research is under investigation by the authors: ongoing experimental studies should provide results to be compared with the numerical predictions. Finally, the thermodynamic approach presented in this work concerns only polymer samples, and will be extended to the case of polymer matrix composites.

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