

# Accounting for differential swelling in the multi-physics modelling of the diffusive behaviour of a tubular polymer structure

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## Abstract

Polymers absorb moisture when exposed to humidity. So-called anomalies of diffusion (i.e. discrepancies from the typical fickian behavior) may occur. Multi-physics diffusion models constitute a possible way for representing such anomalies of diffusion. The purpose of this paper is to take into account the derivative by moisture content of polymer volume in order to establish a diffusion law within the so-called “thermodynamical approach” for a polymer material which experiences a hygro-mechanical load. In this study, the specific case of a tubular structure submitted to either symmetrical or unsymmetrical pressure conditions was investigated.

**Keywords:** *moisture absorption, thermodynamical approach, multiphysics model, tubular structure, differential swelling.*

## 1. Introduction

Polymers and polymeric composites absorb moisture when exposed to ambient humidity or immersed in liquid. Polymeric matrix composites differ from other materials in the sense that low-molecular weight substances such as water may easily migrate even at room temperature, generating a variation of the material’s structure, morphology, and composition. Moreover, many authors have reported that hygro-thermal ageing could induce a loss of the mechanical stiffness and/or strength of organic matrix composites (Selzer et al., 1997; Patel et al., 2002). It is probable that the factors described above will also affect the moisture sorption behavior of polymer matrix composites. In order to predict the time-dependent evolution of the moisture content of composite structures, various models have been developed in the literature. Among them, some are based on the classical Fickian diffusion model (Shen and Springer, 1976; Jacquemin et al., 2002; Jedidi et al., 2005; Gigliotti et al., 2007). More recently, Fick’s model has successfully been combined with scale transition models such as the Eshelby-Kröner self-consistent model for predicting multi-scale distribution of the internal mechanical states during the transient step of the moisture diffusion process experienced by polymer composites (Fréour et al., 2005; Jacquemin et al., 2009).

Nevertheless, some experimental data demonstrate that the moisture sorption in composite structures could differ from the typical Fickian uptake (Cai and Weitsman, 1994; Rao et al., 1995). These discrepancies from the ideal fickian diffusion have been called “anomalies of diffusion”. As a consequence, some researchers have developed models in order to reproduce the anomalous sorption curves observed in practice (Carter and Kibler, 1978; Verpoest and Springer, 1988). Among the proposed methods, (Roy, 1999) documented a multi-physics approach to the diffusion

mechanisms, compatible with the thermodynamics. The approach is similar to that presented by Larché and Cahn or Aifantis and Gerberich for predicting the diffusion of gases through elastic solids (Larché and Cahn, 1973; Aifantis and Gerberich, 1977a; Aifantis and Gerberich, 1977b). The multiphysics thermodynamic model proposed by Larché and Cahn was later implemented by Neogi et al. who achieved the successful fitting of experimental results obtained on thin polymer membranes (Neogi et al., 1986). Nevertheless, in these pioneering works, the differential swelling was treated using simplifying assumptions relating the deformation field to the existing penetrant concentration (Larché and Cahn, 1982).

More recently, other mutliphysics model coupling the mechanical states to mass-transport processes were developed for linear viscoelastic solids (Carbonell and Sarti, 1990). An important feature of that formulation, although limited to the one-dimensional case, is that the expressions used for the chemical potential and the constitutive stress equations are thermodynamically consistent, since they come from the equation describing the Helmholtz free energy (Carbonell and Sarti, 1990).

In recent works (Derrien et al., 2009; Sar et al., 2012), other models, focused on the description of anomalous diffusion, were also developed which were compatible with the thermodynamics. The corresponding mathematical formalism, which historically did not enable the effects of an in-depth heterogeneous profile of the hygro-elastic strains on moisture kinetics to be analyzed, was thereafter improved in order to address this issue (Sar et al., 2013).

This paper is focused on applying the multiphysics model to a cylindrical coordinate system, in order to enable the case of a tubular polymeric structure to be numerically investigated. Actually, in the field of polymer and reinforced polymers, tubular specimens are often used instead of parallelepipeds. Besides, the inner and outer surfaces of tubular structures can relatively easily be submitted to strongly heterogeneous pressures, whereas such a mechanical loading cannot be applied (in static) to a plate. Practical applications are, as an exemple the so called filament wound pressure vessels, which may be submitted to hygro-mechanical loads (Parnas and Katirci, 2002 ; Perreux et al., 2002).

The developments detailed in this paper will extend the formalism, so that an unsymmetrical load (either or both the internal and external boundary conditions for the applied mechanical pressure as well as for the relative humidity can actually be different in the case of a infinitely long tube) can be considered, whereas only symmetrical cases could be modeled using the historical version of the model (Derrien et al., 2009; Sar et al., 2012), and in the original pioneering papers published in this field of research (Larché and Cahn, 1973; Aifantis, 1977).

## 2. Multiphysics diffusion model

Generally, the diffusion equation is deduced from the conservation of mass equation (Larché and Cahn, 1982) in which the first derivative of moisture content with respect to time,  $\dot{C} = \frac{\partial C}{\partial t}$ , relates to the diffusion flux of moisture,  $J_{i,j}$ , as follows:

$$\dot{C} + J_{i,i} = 0 \tag{1}$$

In equation (1), mass transport results from the molecular motion of the penetrant moisture only. This implies that the model developed in the following of the paper is appropriate in the case when small penetrant concentrations are considered. Indeed, in the general case, when high concentrations of the penetrants are expected to occur, in addition to transport by molecular motion (diffusion), mass may also be transported by the bulk motion of the penetrant fluid itself, resulting in a convective term proportional to the velocity of the fluid. This convective term adds to the diffusion term in the constitutive equation defining the mass flux. The interested reader can refer to the comprehensive textbook written by Bird et al. (2007).

In the present work, the diffusion flux of moisture will be written in terms of the chemical potential of water  $\tilde{\mu}_w$  as proposed, for instance, in (Neogi et al., 1986):

$$J_i = - \frac{D C}{R T} \text{grad } \tilde{\mu}_w \quad (2)$$

Where  $D$  is the diffusion coefficient in  $[\text{mm}^2/\text{s}]$ ,  $R$  is the gas constant in  $[\text{J}/(\text{mol.K})]$ , and  $T$  the absolute temperature  $[\text{K}]$ .

Actually, the main objective of the present paper consists in finding the time and space dependent moisture content. As a consequence, it is mandatory to focus on determining the analytical expression satisfied by the chemical potential of water  $\tilde{\mu}_w$ .

### 3. General expression of the chemical potential of water

For the sake of simplicity, the following mathematical development of the present work will be limited to equilibrium thermodynamics. Consequently, the resulting model is strictly suitable only for rubbery polymers. The rigorous treatment of the nonequilibrium nature of glassy polymers would actually require accounting for more complex expressions of the chemical potential, derived from non-equilibrium thermodynamics. The required expression for the corresponding Gibbs free energy in the context of low molecular weight species diffusing glassy polymers has been derived by Doghieri and Sarti (1996) from the pioneering paper of Sanchez and Lacombe (1978).

The chemical potential of water  $\tilde{\mu}_w$  is defined as the partial derivative of the Helmholtz free energy,  $F = F_0 + n f_w(C) + V_\epsilon W$ , with respect to the amount of water  $n_w$ . Where  $F_0$  is the constant free energy of the dry stress-free polymer,  $f_w(C)$  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. Its first derivative by the moisture content will be denoted by the variable  $f'_w(C) = \frac{\partial [f_w(C)]}{\partial C}$ .  $n$  and  $V_\epsilon$  are respectively the amount of polymer and its volume at any stage (thus, possibly depending on the strain  $\epsilon$ ), whereas  $W$  denotes the hydro-elastic strain energy (Derrien et al., 2009). In the present study, the amount of polymer is assumed to remain constant throughout the diffusion process, thus  $\frac{\partial n}{\partial C} = 0$ :

$$\tilde{\mu}_w(C) = \frac{\partial F}{\partial n_w} = \frac{\partial F}{\partial C} \frac{\partial C}{\partial n_w} = \left[ \frac{\partial F_0}{\partial C} + n f'_w(C) + W \frac{\partial V_\epsilon}{\partial C} + V_\epsilon \frac{\partial W}{\partial C} \right] \frac{\partial C}{\partial n_w} \quad (3)$$

W corresponds to the hygro-elastic strain energy. For simplicity, the present work will be limited to structures made of a macroscopically isotropic polymer. As a consequence, the hygro-elastic strain energy can be written as a function of both the bulk modulus k and shear modulus G:

$$W = \frac{1}{2} \boldsymbol{\sigma} : \boldsymbol{\varepsilon}^{\text{el}} = \frac{k}{2} (\text{tr } \boldsymbol{\varepsilon} - 3 \eta C)^2 + G \mathbf{e} : \mathbf{e} \quad (4)$$

Where  $\boldsymbol{\varepsilon}^{\text{el}}$  is the elastic strain,  $\boldsymbol{\varepsilon}$  being the total strain, whereas  $\mathbf{e}$  is the deviatoric strain tensor.

The following sections will be focused on determining expressions for the mechanical states as well as for the various derivatives involved in expressions (3-4) above.

## 4. Mechanical states experienced by a tubular structure submitted to a hygro-mechanical load

### 4.1 Introduction

As presented previously in the introduction, the multiphysics diffusion model the general form of which is given in section 2 above, was historically expressed for plate specimen geometry only (Derrien et al., 2009; Sar et al., 2012; Sar et al., 2013). Nevertheless, tubular geometry is interesting, since it is possible to apply heterogeneous internal and external boundary conditions on them. Actually, both the mechanical pressure and relative humidity experienced by the inner boundary can differ from those applied to the outer boundary of a supposedly infinitely long tube. This paper is devoted to study the effects of the tubular geometry of a polymer structure on the moisture diffusion process. The tube is assumed to be submitted to the following mechanical boundary condition: pressures  $p_1$  and  $p_2$ , are respectively applied to the internal surface or the external surface. Besides, as stated in the introduction, the heterogeneous radial distribution of the moisture content during (at least) the transient phase of the moisture diffusion process. As a consequence, a radial differential swelling takes place in the depth of the tubular structure, leading to the existence of an internal hygroscopic pressure  $P_{\text{is}}$ .

In the present work, the stress state experienced by the polymer results from the sum of i) a mechanical pressure, induced by the mechanical boundary condition and ii) a hygroscopic pressure  $P_{\text{is}}$  resulting from the differential swelling induced by the application of environmental hygroscopic boundary conditions:

$$\boldsymbol{\sigma}_{ij} = \begin{pmatrix} \sigma_{rr}^{\text{mec}} & 0 & 0 \\ 0 & \sigma_{\theta\theta}^{\text{mec}} & 0 \\ 0 & 0 & \sigma_{zz}^{\text{mec}} \end{pmatrix} + \begin{pmatrix} -P_{\text{is}} & 0 & 0 \\ 0 & -P_{\text{is}} & 0 \\ 0 & 0 & -P_{\text{is}} \end{pmatrix} = \begin{pmatrix} \sigma_{rr}^{\text{mec}} - P_{\text{is}} & 0 & 0 \\ 0 & \sigma_{\theta\theta}^{\text{mec}} - P_{\text{is}} & 0 \\ 0 & 0 & \sigma_{zz}^{\text{mec}} - P_{\text{is}} \end{pmatrix} \quad (5)$$

The trace of the stress tensor (5) can be written as follows:

$$\text{tr} \boldsymbol{\sigma}_{ij} = \sigma_{rr}^{\text{mec}} + \sigma_{\theta\theta}^{\text{mec}} + \sigma_{zz}^{\text{mec}} - 3P_{\text{is}} \quad (6)$$

## 4.2 Purely mechanical part of the stress and strain states experienced by the polymer tube

In the present work, the so-called “purely mechanical stresses” are due to the application of pressures  $p_1$  and  $p_2$ , respectively, to the internal surface or the external surface of the tube. This obviously excludes the mechanical states induced by moisture diffusion, the contribution of which will be expressed in section 4.3 below. Thus, the purely mechanical states are deduced from the equilibrium equations:

$$\frac{\partial \sigma_{rr}^{\text{mec}}}{\partial r} + \frac{\sigma_{rr}^{\text{mec}} - \sigma_{\theta\theta}^{\text{mec}}}{r} = 0 \quad (7)$$

Equation (7) admits the following solutions:

$$\begin{cases} \sigma_{rr}^{\text{mec}} = \frac{1}{R_2^2 - R_1^2} \left( p_1 R_1^2 - p_2 R_2^2 - (p_1 - p_2) \frac{R_2^2 R_1^2}{r^2} \right) \\ \sigma_{\theta\theta}^{\text{mec}} = \frac{1}{R_2^2 - R_1^2} \left( p_1 R_1^2 - p_2 R_2^2 + (p_1 - p_2) \frac{R_2^2 R_1^2}{r^2} \right) \\ \sigma_{zz}^{\text{mec}} = 2\nu \frac{p_1 R_1^2 - p_2 R_2^2}{R_2^2 - R_1^2} \end{cases} \quad (8)$$

Where  $R_1$ ,  $R_2$  respectively denotes the internal and external radius of the studied structure, whereas  $\nu$  stands for the Poisson's ratio of the polymer.

By combining expressions (8) in relation (6), one obtains the following interesting property for:

$$\sigma_{rr}^{\text{mec}} + \sigma_{\theta\theta}^{\text{mec}} + \sigma_{zz}^{\text{mec}} = 2(1 + \nu) \frac{p_1 R_1^2 - p_2 R_2^2}{R_2^2 - R_1^2} = A \quad (9)$$

In expression (9) above,  $A$  is a constant term, independent from the position in the tube (specifically, from the radial position  $r$ ).

In this work, the length of the studied tubular structure is considered to be very large compared to its thickness. As a consequence the normal strain  $\epsilon_{zz}^{\text{mec}}$  is constrained by nearby material and is small compared to the cross-sectional strains. As a result, plane strain will be considered as an acceptable approximation in the present study. Accounting for this additional simplifying condition, the strain tensor experienced by the polymer due to the mechanical pressure satisfies the following form:

$$\varepsilon_{ij}^{\text{mec}} = \begin{pmatrix} \varepsilon_{rr}^{\text{mec}} & 0 & 0 \\ 0 & \varepsilon_{\theta\theta}^{\text{mec}} & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (10)$$

Considering a purely elastic Hooke's law, the strain states induced by the external pressures, resulting from the initial forms (8) satisfy the following expressions, where  $E$  stands for the Young's modulus of the isotropic polymer:

$$\begin{cases} \varepsilon_{rr}^{\text{mec}} = \frac{1+\nu}{E} \frac{1}{R_2^2 - R_1^2} \left( (1-2\nu)(p_1 R_1^2 - p_2 R_2^2) - (p_1 - p_2) \frac{R_2^2 R_1^2}{r^2} \right) \\ \varepsilon_{\theta\theta}^{\text{mec}} = \frac{1+\nu}{E} \frac{1}{R_2^2 - R_1^2} \left( (1-2\nu)(p_1 R_1^2 - p_2 R_2^2) + (p_1 - p_2) \frac{R_2^2 R_1^2}{r^2} \right) \end{cases} \quad (11)$$

### 4.3 Hygroscopic pressure

Moisture absorption induces swelling strains that actually correspond to the existence of a hygroscopic pressure  $P_{is}$  within the material, previously introduced in relation (5). One of the main issues of the present work consists in finding the expression satisfied by that quantity of interest. The knowledge of  $P_{is}$  is actually mandatory for determining the unknown distribution of the internal strains within the depth of the tubular specimen. Consecutively this would enable to evaluate both the elastic strain energy  $W$  and its first derivative by the moisture content  $\frac{\partial W}{\partial C}$

appearing in the general expression for the chemical potential of water (3).

The in-depth, time-dependent hygroscopic pressure profile occurring during the transient stage of the diffusion process is determined by expressing the spatial laplacian ( $\Delta$ ) of the trace of the stress tensor experienced by the polymer, according to the line of reasoning presented in (Sar et al., 2012). One eventually obtains:

$$\Delta \text{tr} \sigma_{ij} = -2\eta \frac{E}{1-\nu} \Delta C \quad (12)$$

Where  $\eta$  is the Coefficient of Moisture Expansion (CME) of the polymer, whereas  $\Delta C$  stands for the Laplacian of moisture content.

In the present work, the trace of stress tensor  $\text{tr} \sigma_{ij}$  is given by expressions (6, 9):  $\text{tr} \sigma_{ij} = A - 3 P_{is}$  where  $A$  was found to be a uniform term (independent from the position in the tube). Thus,  $\Delta A = 0$ . Equation (12) can eventually be reduced to:

$$\Delta P_{is} = \frac{2E}{3(1-\nu)} \eta \Delta C = \frac{\alpha}{A_0} \eta \Delta C \quad (13)$$

Where the ratio  $\frac{\alpha}{A_0} = \frac{2E}{3(1-\nu)}$ , was previously defined in (Sar et al., 2012).from the parameters

$$A_0 = \frac{3\omega_w}{RT\rho_0} \text{ and } \alpha = \frac{2E}{(1-\nu)} \frac{\omega_w}{RT\rho_0} . \omega_w \text{ stands for the molar mass of water, whereas } \rho_0 \text{ is the}$$

density of the polymer at the initial (strain-free) state. R is the ideal gas constant and T the absolute temperature.

The development of expression (13) for the spatial Laplacian of the hygroscopic pressure, expressed in cylindrical coordinates yields the following form:

$$\Delta P_{is} = \frac{\alpha}{A_0} \eta \Delta C = \frac{\alpha}{A_0} \eta \left( \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{1}{r^2} \frac{\partial^2 C}{\partial \theta^2} + \frac{\partial^2 C}{\partial z^2} \right) \quad (14)$$

In the present work, we consider a cylinder, whose length is large compared to its thickness. As a consequence, the diffusion is considered to occur only in the radial direction r, so the unidirectional solution of equation (14) satisfies the following form:

$$\Delta P_{is} = \frac{\alpha}{A_0} \eta \left( \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right) \quad (15)$$

The left-hand side of expression (33) can be rewritten owing to the definition of the Laplacian in cylindrical coordinates, and then factorized as follows:

$$\frac{\partial^2 P_{is}}{\partial r^2} + \frac{1}{r} \frac{\partial P_{is}}{\partial r} = \frac{\alpha}{A_0} \eta \left( \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right) \Leftrightarrow \frac{\partial^2}{\partial r^2} \left( P_{is} - \frac{\alpha}{A_0} \eta C \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( P_{is} - \frac{\alpha}{A_0} \eta C \right) = 0 \quad (16)$$

In order to solve equation (16), let us introduce a changes of variables:  $u = P_{is} - \frac{\alpha}{A_0} \eta C$ ;  $m = \frac{\partial u}{\partial r}$ .

Expression (16) thus transforms as follows:

$$\frac{\partial^2 u}{\partial r^2} + \frac{1}{r} \frac{\partial u}{\partial r} = 0 \Leftrightarrow \frac{\partial m}{\partial r} + \frac{1}{r} m = 0 \quad (17)$$

By integrating the partial differential equations (17) over the variable r we obtain the following expression for the quantity u:

$$u = \int m.dr = \int \frac{\lambda_1}{r}.dr = \lambda_1 \ln r + \lambda_2 \quad (18)$$

With  $\lambda_1$  and  $\lambda_2$  two unknowns to be determined in the following part of this paper.

As a result, introducing (18) in (17) provides the following general form for the hygroscopic pressure in the considered case:

$$P_{is} = \frac{\alpha}{A_0} \eta C(r, t) + \lambda_1 \ln r + \lambda_2 \quad (19)$$

In order to determine the constants  $\lambda_1$  and  $\lambda_2$  appearing in the expression of the hygroscopic pressure  $P_{is}$ , the following conditions will be used, namely i) a net axial force of zero, ii) bending moment null:

$$\begin{cases} \int_{R_1}^{R_2} 2 \pi P_{is} r \, dr = 0 \\ \int_{R_1}^{R_2} 2 \pi P_{is} r^2 \, dr = 0 \end{cases} \quad (20)$$

By considering the general form (19) previously established for the hygroscopic pressure, the conditions (20) can be expressed as follows:

$$\begin{cases} \frac{\alpha}{A_0} \eta J_1 + \lambda_1 \left( \frac{R_2^2 \ln R_2 - R_1^2 \ln R_1}{2} - \frac{R_2^2 - R_1^2}{4} \right) + \lambda_2 \frac{R_2^2 - R_1^2}{2} = 0 \\ \frac{\alpha}{A_0} \eta J_2 + \lambda_1 \left( \frac{R_2^3 \ln R_2 - R_1^3 \ln R_1}{3} - \frac{R_2^3 - R_1^3}{9} \right) + \lambda_2 \frac{R_2^3 - R_1^3}{3} = 0 \end{cases} \quad (21)$$

Where the variables  $J_1$  and  $J_2$  respectively correspond to the following integrals:

$$J_1 = \int_{R_1}^{R_2} r C(r, t) \, dr \quad ; \quad J_2 = \int_{R_1}^{R_2} r^2 C(r, t) \, dr \quad (22)$$

The reader should take care of the fact that solving equation (21) above requires the knowledge of the in-depth profile of the moisture content at the specific time  $t$  corresponding to the calculation, since that quantity explicitly appears in the integrals  $J_1, J_2$  defined by (22).

The system of 2 equations (21) with 2 unknowns, namely  $\lambda_1$  and  $\lambda_2$ , previously obtained admits the following set of solutions:

$$\lambda_1 = - \frac{\frac{\alpha}{A_0} \eta \left( 12 J_1 [R_2^3 - R_1^3] - 18 J_2 [R_2^2 - R_1^2] \right)}{6 R_1^2 R_2^2 (R_1 - R_2) \ln \frac{R_1}{R_2} - (R_2^2 - R_1^2) (R_2^3 - R_1^3)} \quad (23)$$



$$\lambda_2 = -\frac{\frac{\alpha}{A_0} \eta \left\{ J_1 \left( 12 \left[ R_2^3 \ln R_2 - R_1^3 \ln R_1 \right] - 4 \left[ R_2^3 - R_1^3 \right] \right) - J_2 \left( 18 \left[ R_2^2 \ln R_2 - R_1^2 \ln R_1 \right] - 9 \left[ R_2^2 - R_1^2 \right] \right) \right\}}{6 R_1^2 R_2^2 (R_2 - R_1) \ln \frac{R_1}{R_2} + (R_2^2 - R_1^2) (R_2^3 - R_1^3)} \quad (24)$$

The expressions obtained for the mechanical states experienced by the polymer tubular structure submitted to an external pressure during the transient part of the moisture diffusion process enable to explicit the chemical potential of water.

## 5. Finding a closed-form solution for the chemical potential of water

### 5.1 First derivative of the moisture content in the polymer by the amount of water

The moisture content in the polymer is calculated through the ratio  $C = \frac{n_w \omega_w}{n \omega}$ , here  $\omega_w, \omega$  stand for respectively the molar mass of water and polymer. As a consequence, one immediately finds the first derivative of the moisture content by the amount of water:

$$\frac{\partial C}{\partial n_w} = \frac{\partial}{\partial n_w} \left( \frac{n_w \omega_w}{n \omega} \right) = \frac{1}{n} \frac{\omega_w}{\omega} \quad (25)$$

### 5.2 Volume occupied by the polymer during the moisture diffusion process

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, through:

$$\frac{V_\varepsilon}{V_0} = \frac{\rho_0}{\rho_\varepsilon} = \text{tr } \boldsymbol{\varepsilon} + 1 \quad (26)$$

Where  $V_\varepsilon, V_0 = \frac{n \omega}{\rho_0}, \rho_0, \rho_\varepsilon$  stand respectively for the polymer volume and its density at present (strained) and initial (strain-free) states.

$$\frac{\partial V_\varepsilon}{\partial C} = \frac{\partial V_\varepsilon}{\partial \text{tr } \boldsymbol{\varepsilon}} \frac{\partial \text{tr } \boldsymbol{\varepsilon}}{\partial C} = V_0 \frac{\partial \text{tr } \boldsymbol{\varepsilon}}{\partial C} = \frac{n \omega}{\rho_0} \frac{\partial \text{tr } \boldsymbol{\varepsilon}}{\partial C} \quad (27)$$

Let us examine in more detail the partial derivative  $\frac{\partial \text{tr } \boldsymbol{\varepsilon}}{\partial C}$  appearing in relation (27), above.

The strain experienced by the polymer is assumed to respect the classical hygro-elastic Hooke's law:

$$\varepsilon_{ij} = \frac{1+\nu}{E} \sigma_{ij} - \frac{\nu}{E} \text{tr } \boldsymbol{\sigma}_{ij} \delta_{ij} + \eta C \delta_{ij} \quad (28)$$

By combining (5), (8) and (28), the trace of the strain tensor expressed as a function of the moisture content can be written as follows:

$$\text{tr } \varepsilon = \frac{A - 3P_{1s}}{3k} + 3\eta C \quad (29)$$

Since  $A$  is a constant term in (29), the first partial derivative of the strain tensor by the moisture content is actually dependent on the first partial derivative of the hygroscopic pressure with respect to the moisture content. The hygroscopic pressure experienced by the polymer during the moisture diffusion process satisfies the form (19) established previously in the present work. One eventually finds:

$$\frac{\partial \text{tr } \varepsilon}{\partial C} = -\frac{1}{k} \frac{\partial P_{1s}}{\partial C} + 3\eta = -\frac{1}{k} \frac{\partial}{\partial C} \left( \frac{\alpha}{A_0} \eta C + \lambda_1 \ln r + \lambda_2 \right) + 3\eta = \eta \frac{3A_0 k - \alpha}{A_0 k} \quad (30)$$

Expression (50) above enables the first partial derivative by the moisture content of the volume occupied by the polymer to be determined:

$$\frac{\partial V_\varepsilon}{\partial C} = V_0 \frac{\partial \text{tr } \varepsilon}{\partial C} = \frac{n \omega}{\rho_0} \eta \frac{3A_0 k - \alpha}{A_0 k} \quad (31)$$

### 5.3 Hygro-elastic strain energy

The first derivative, with respect to the moisture content, of the hygro-elastic strain energy (4) can be written as follows:

$$\begin{aligned} \frac{\partial W}{\partial C} &= \frac{\partial}{\partial C} \left[ \frac{k}{2} (\text{tr } \varepsilon - 3\eta C)^2 + G \mathbf{e} : \mathbf{e} \right] \\ &= \frac{1}{2} (\text{tr } \varepsilon - 3\eta C)^2 \frac{\partial k}{\partial C} + k (\text{tr } \varepsilon - 3\eta C) \left[ \frac{\partial (\text{tr } \varepsilon)}{\partial C} - 3\eta \right] + G \frac{\partial (\mathbf{e} : \mathbf{e})}{\partial C} + \mathbf{e} : \mathbf{e} \frac{\partial G}{\partial C} \end{aligned} \quad (32)$$

The following subsections (from 5.3.1 to 5.3.2) will be devoted to the determination of the following terms, necessary to explicit relation (32), namely,  $\frac{\partial k}{\partial C}$ ,  $\frac{\partial G}{\partial C}$ ,  $\mathbf{e} : \mathbf{e}$  and  $\frac{\partial}{\partial C} (\mathbf{e} : \mathbf{e})$ .

#### 5.3.1 Plasticization of the polymers

One of the main effects of water on polymer matrices is plasticization (Chang et al., 2000; Patel et al., 2002; Mali et al., 2005; Myllytie et al., 2010).

Water molecules can be sorbed in different ways in polymers. Water can either be dispersed in the matrix (random dispersion of free, unbound molecules in the bulk of the matrix) or be associated to specific sites of the macromolecular backbone, through hydrogen bonding or polar interactions (McBrierty et al., 1999). Both sorption mechanisms induce a reversible reduction of both the glass

transition of the polymer and its mechanical properties such as the Young's modulus (Nielsen and Toftegaard, 2000; Yakimets et al., 2007). It is probable that such an evolution of the elastic stiffness experienced by the polymer could affect its moisture sorption behavior as well as the resulting internal mechanical states, as predicted in a recent theoretical study (Youssef et al., 2009).

However, in the present work, the elastic stiffness of the polymer is assumed to remain independent from the moisture content, i.e. the model disregards the plasticization which effectively occurs in practice during the diffusion of moisture. Consequently, the following additional simplifying assumptions will be considered to be satisfied for the partial derivatives of the bulk modulus and the Coulomb modulus by the moisture content:  $\frac{\partial k}{\partial C} = 0$  and  $\frac{\partial G}{\partial C} = 0$ .

### 5.3.2 Deviatoric part of the strain tensor

The deviatoric part of the hygro-elastic strain tensor experienced by the polymer, which appears in the form satisfied by the hygro-elastic energy (4), is given by the following expression:

$$e_{ij} = \varepsilon_{ij} - \frac{1}{3} \text{tr} \varepsilon_{ij} \delta_{ij} = \frac{1}{2G} \sigma_{ij} - \frac{1}{6G} \text{tr} \sigma_{ij} \delta_{ij} \quad (33)$$

The right-hand side of expression (33) was obtained accounting for the relations (29).

The contracted product of the deviatoric part of the strain tensor by itself can be deduced from its definition (35), by introducing the classical replacement rule for the contracted product of the kronecker by the stress tensor ( $\delta_{ij} : \sigma_{ij} = \sigma_{ij} : \delta_{ij} = \text{tr} \sigma_{ij}$ ):

$$e_{ij} : e_{ij} = \frac{1}{4G^2} \left( \sigma_{ij} : \sigma_{ij} - \frac{1}{3} (\text{tr} \sigma_{ij})^2 \right) = \frac{1}{4G^2} \left( \left( \sigma_{rr}^{\text{mec}} \right)^2 + \left( \sigma_{\theta\theta}^{\text{mec}} \right)^2 + \left( \sigma_{zz}^{\text{mec}} \right)^2 - \frac{1}{3} \left( \sigma_{rr}^{\text{mec}} + \sigma_{\theta\theta}^{\text{mec}} + \sigma_{zz}^{\text{mec}} \right)^2 \right) \quad (35)$$

The right hand side of (35) is obtained accounting for the explicit form of the stress tensor (5).

The form (35) above admits a derivative by the moisture content which is null:

$$\frac{\partial (e_{ij} : e_{ij})}{\partial C} = \frac{\partial (e : e)}{\partial C} = 0 \quad (36)$$

### 5.3.3 Consequences

Accounting for the hypotheses and developments described in paragraphs 5.3.1 and 5.3.2, the first derivative, by the moisture content, of the hygro-elastic strain energy (32) simplifies as follows:

$$\frac{\partial W}{\partial C} = k(\text{tr} \varepsilon - 3\eta C) \left[ \frac{\partial (\text{tr} \varepsilon)}{\partial C} - 3\eta \right] = k(\text{tr} \varepsilon - 3\eta C) \left[ \eta \frac{3A_0 k - \alpha}{A_0 k} - 3\eta \right] = -\eta \frac{\alpha}{A_0} (\text{tr} \varepsilon - 3\eta C) \quad (37)$$

## 5.4 Closed form solution for the chemical potential

The introduction of replacement rules (25), (31) and (37) in the general form (3) yields the following expression for the chemical potential:

$$\tilde{\mu}_w(\mathbf{C}) = \left[ n f'_w(\mathbf{C}) + W \frac{n \omega}{\rho_0} \eta \frac{3 A_0 k - \alpha}{A_0 k} - \eta \frac{\alpha}{A_0} (\text{tr } \boldsymbol{\varepsilon} - 3 \eta \mathbf{C}) V_\varepsilon \right] \frac{1}{n} \frac{\omega_w}{\omega} \quad (38)$$

According to expressions (4), (26), and considering that  $\frac{\omega_w}{\omega} f'_w(\mathbf{C}) = \mu_0 + RT \ln \frac{\mathbf{C}}{C_0}$ , the relation previously obtained for the expression of the chemical potential (38) can be developed as follows:

$$\begin{aligned} \tilde{\mu}_w(\text{tr } \boldsymbol{\varepsilon}, \mathbf{C}) = & \mu_0 + R T \ln \frac{\mathbf{C}}{C_0} - 3 \eta \frac{k \omega_w}{\rho_0} (\text{tr } \boldsymbol{\varepsilon} - 3 \eta \mathbf{C})(\text{tr } \boldsymbol{\varepsilon} + 1) + \frac{\eta \omega_w}{A_0 \rho_0} (3 A_0 k - \alpha)(\text{tr } \boldsymbol{\varepsilon} - 3 \eta \mathbf{C})(\text{tr } \boldsymbol{\varepsilon} + 1) + \\ & + \frac{\omega_w}{\rho_0} \left( \frac{k}{2} (\text{tr } \boldsymbol{\varepsilon} - 3 \eta \mathbf{C})^2 + G e : e \right) \eta \frac{3 A_0 k - \alpha}{A_0 k} \end{aligned} \quad (39)$$

## 6. Diffusion equation of the multiphysics model

We obtain the constitutive equation by using the mass conservation equation (1) in which the chemical potential of water has been written as a function of both the trace of the strains and the moisture content:

$$\dot{\mathbf{C}} = \frac{D}{RT} \text{div} \left[ \mathbf{C} \left( \overset{\rightarrow}{\text{grad}} \tilde{\mu}_w(\mathbf{C}, \text{tr } \boldsymbol{\varepsilon}) \right) \right] = \frac{D}{RT} \text{div} \left[ \mathbf{C} \left( \frac{\partial \tilde{\mu}_w}{\partial \mathbf{C}} \overset{\rightarrow}{\text{grad}} \mathbf{C} + \frac{\partial \tilde{\mu}_w}{\partial \text{tr } \boldsymbol{\varepsilon}} \overset{\rightarrow}{\text{grad}} \text{tr } \boldsymbol{\varepsilon} \right) \right] \quad (40)$$

According to (40), it is thus necessary to determine the first partial derivative of the chemical potential of water from (39), with respect to either the moisture content or the trace of the strain tensor. One can write:

$$\frac{\partial \tilde{\mu}_w}{\partial \mathbf{C}} = \frac{R T}{C} + \frac{9 \eta^2 \omega_w k}{\rho_0} (\text{tr } \boldsymbol{\varepsilon} + 1) - \frac{3 \eta^2 \omega_w}{A_0 \rho_0} (3 A_0 k - \alpha)(2 \text{tr } \boldsymbol{\varepsilon} - 3 \eta \mathbf{C} + 1) \quad (41)$$

The partial derivatives of the chemical potential by the strain trace  $\text{tr } \boldsymbol{\varepsilon}$  can be written as:

$$\frac{\partial \tilde{\mu}_w}{\partial \text{tr } \boldsymbol{\varepsilon}} = - \frac{3 k \omega_w \eta}{\rho_0} (2 \text{tr } \boldsymbol{\varepsilon} - 3 \eta \mathbf{C} + 1) + \frac{\eta \omega_w}{A_0 \rho_0} (3 A_0 k - \alpha)(3 \text{tr } \boldsymbol{\varepsilon} - 6 \eta \mathbf{C} + 1) \quad (42)$$

Let us introduce in the equation (40) describing the moisture transport, the expressions (41) and (42) obtained for the first partial derivatives of the chemical potential of water with respect to

either the moisture content or the trace of the strain. Using the replacement rule  $A_0 = \frac{3\omega_w}{RT\rho_0}$ , one eventually obtains the following development:

$$\begin{aligned} \dot{C} = D \operatorname{div} & \left( \left( 1 + 3A_0 \eta^2 k C (\operatorname{tr} \varepsilon + 1) \right) \vec{\operatorname{grad}} C - A_0 k \eta C (2 \operatorname{tr} \varepsilon - 3 \eta C + 1) \vec{\operatorname{grad}} \operatorname{tr} \varepsilon \right) + \\ & + D \frac{\eta (3A_0 k - \alpha)}{3} \operatorname{div} \left( -3 \eta C (2 \operatorname{tr} \varepsilon - 3 \eta C + 1) \vec{\operatorname{grad}} C + C (3 \operatorname{tr} \varepsilon - 6 \eta C + 1) \vec{\operatorname{grad}} \operatorname{tr} \varepsilon \right) \end{aligned} \quad (43)$$

Expression (43) can be simplified. The resulting time-dependent diffusive behavior for a polymer cylinder subjected to an unsymmetrical humid ambient load is given as follows:

$$\dot{C} = D \left[ \begin{aligned} & \left( 1 + V_1 \eta^2 C + V_2 \eta^3 C^2 + \xi N_1 \right) \frac{\partial^2 C}{\partial r^2} + \left( 1 + V_1 \eta^2 C + V_2 \eta^3 C^2 + \xi (N_1 + N_2) + Q_1 \lambda_1 \right) \frac{1}{r} \frac{\partial C}{\partial r} + \\ & + \left( \eta^2 (V_1 + V_3 C) + \xi N_3 \right) \left( \frac{\partial C}{\partial r} \right)^2 + \left( \frac{3\xi}{k} + Q_2 \right) \lambda_1^2 \frac{1}{r^2} C \end{aligned} \right] \quad (44)$$

The expressions for the factors  $V_1$ ,  $V_2$ ,  $V_3$ ,  $Q_1$ ,  $Q_2$ ,  $N_1$ ,  $N_2$ ,  $N_3$  and  $\xi$  are given in appendix A.

## 7. Boundary conditions for a cylindrical structure

The boundary condition is obtained by equating the chemical potential of water in humid air,  $\hat{\mu}_w = \hat{\mu}_0 + RT \ln \frac{p_w}{p_0}$  (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  $p_w$ ), with the generalized chemical potential of the polymer,  $\tilde{\mu}_w$ , the expression for which is given by equation (39) in the present work. This statement yields the following equation:

$$\begin{aligned} \hat{\mu}_0 + R T \ln \frac{p_w}{p_0} = \mu_0 + R T \ln \frac{C}{C_0} - \frac{3 \eta \omega_w k}{\rho_0} (\operatorname{tr} \varepsilon - 3 \eta C)(\operatorname{tr} \varepsilon + 1) + \\ + \frac{\eta \omega_w}{A_0 \rho_0} (3 A_0 k - \alpha) (\operatorname{tr} \varepsilon - 3 \eta C)(\operatorname{tr} \varepsilon + 1) + \\ + \frac{\omega_w}{\rho_0} \left( \frac{k}{2} (\operatorname{tr} \varepsilon - 3 \eta C)^2 + G e : e \right) \eta \frac{3 A_0 k - \alpha}{A_0 k} \end{aligned} \quad (45)$$

The above form (45) can be simplified as follows:

$$\ln \left( \frac{C}{C_0} \right) = \frac{\hat{\mu}_0 - \mu_0}{R T} + A_0 \eta k (\text{tr } \varepsilon - 3 \eta C)(\text{tr } \varepsilon + 1) - \frac{\eta}{3} (3 A_0 k - \alpha)(\text{tr } \varepsilon - 3 \eta C)(\text{tr } \varepsilon + 1) - \frac{A_0}{3} \left( \frac{k}{2} (\text{tr } \varepsilon - 3 \eta C)^2 + G e : e \right) \eta \frac{3 A_0 k - \alpha}{A_0 k} \quad (46)$$

From (46), one can deduce an expression for the required moisture content at the boundary:

$$C = S p_w \exp \left( \frac{\eta}{2} (\alpha - A_0 k)(\text{tr } \varepsilon - 3 \eta C)^2 + \frac{\alpha \eta}{3} (\text{tr } \varepsilon - 3 \eta C)(3 \eta C + 1) - \frac{\eta G}{3 k} (3 A_0 k - \alpha) e : e \right) \quad (47)$$

Where, according to Henry's law,  $S = \frac{C_0}{p_0} \exp \left( \frac{\hat{\mu}_0 - \mu_0}{R T} \right)$ . Besides, the explicit form of the product  $e:e$  has been found previously (35).

Accounting for the expression (29) satisfied by the trace of the strain tensor in (47) yields:

$$C = S p_w \exp \left( \frac{\eta}{2} (\alpha - A_0 k) \left( \frac{A - 3 P_{is}}{3 k} \right)^2 + \frac{\alpha \eta}{3} \left( \frac{A - 3 P_{is}}{3 k} \right) (3 \eta C + 1) - \frac{\eta G}{3 k} (3 A_0 k - \alpha) e : e \right) \quad (48)$$

Thus, according to relation (48) above, the unmodified Henry's law  $C = S p_w$  would be obtained at the boundary when the exponential term tends towards 1. This condition is fulfilled when the coefficient of moisture expansion  $\eta$  is infinitely small.

## 8. Numerical results

### 8.1 Parameters

The numerical simulations correspond to a 4 mm thick tubular structure made of a polymer resin whose internal radius is  $R_1=100$  mm. The polymer structure is subjected to moisture diffusion while experiencing a pressure load. Both surfaces of the cylinder are assumed to be subjected to the same relative humidity, which correspond to a reference moisture content level  $C_0$  of 5 % (in the case that the multiphysics effects are neglected). The mathematical equation governing the diffusion corresponds to equation (44), whereas the boundary condition is obtained using expression (48).

We would like to simulate the moisture absorption within the material described above in the cases when either a symmetrical or an unsymmetrical moisture condition is imposed at the internal or external surfaces of the tube. In order to achieve the computations, input values gathered in table 1 were considered.

## 8.2 Effects of the external pressure

### 8.2.1 Case of a symmetrical external pressure

Figure 1 shows the effect induced by the application of an external symmetrical pressure (i.e.  $p_1 = p_2$ ), varying from 0.1 MPa to 20 MPa, on the time-dependent evolution of the macroscopic (average) moisture content. The Coefficient of Moisture Expansion  $\eta$  used in order to obtain the depicted results is equal to 0.6.

According to figure 1, an increased applied pressure slightly reduces the maximum moisture absorption capacity attained in the permanent regime. Nevertheless, the effect is rather limited in the case that a symmetrical external pressure is considered.

### 8.2.2 Case of a unsymmetrical external pressure

Let us consider now the case when an unsymmetrical external pressure is applied to the cylinder. Figure 2-a was obtained assuming a low internal pressure:  $p_1 = 0.1$  MPa, whereas three values, respectively  $p_2 = 1$  MPa, 10 MPa or 20 MPa, were successively considered for pressure on the external surface of the cylinder. On the contrary, figure 2-b was obtained assuming a low external pressure  $p_2 = 0.1$  MPa, and three values of the internal pressure:  $p_1 = 1$  MPa, 10 MPa or 20 MPa. The Coefficient of Moisture Expansion  $\eta$  used in order to obtain the depicted results is equal to 0.6.

Unlike the numerical results already discussed on figure 1 corresponding to the symmetrical case of pressure, an unsymmetrical external pressure yields significant effects on the diffusion of moisture in the tubular polymer structure as shown in figure 2. The maximum moisture absorption capacity attained in permanent regime strongly depends on the heterogeneity between the internal pressure  $p_1$  and the external pressure  $p_2$ : it increases when  $p_1$  increases and  $p_2$  decreases. Thus, the highest moisture absorption capacity is obtained with high  $p_1$  and low  $p_2$  (see figure 2-b) while the lowest moisture absorption capacity is obtained by applying a low  $p_1$  and a high  $p_2$  (see figure 2-a).

## 8.3 Effects of the coefficient of moisture expansion

Figure 1 shows the time-dependent evolution of the macroscopic (average) moisture content, as a function of the CME:  $\eta = 0$ ;  $\eta = 0.6$  or  $\eta = 1$ , in the case when an imposed symmetrical pressure of 1 MPa is considered.

According to figure 3, the multiphysics model predicts a fickian diffusion process for the case when the coefficient of moisture absorption of the polymer is assumed to be null. Discrepancies from the typical fickian kinetics occur as predicted by the model when  $\eta \neq 0$ . In particular, the apparent moisture diffusion coefficient of the polymer tube (i.e. the slope of the curves drawn on figure 3) varies at the beginning of the diffusion process (i.e. the slope of the curves are not

independent from the ratio  $\frac{\sqrt{t}}{e}$  anymore at the initial stage, when  $t$  tends towards 0), when high values of  $\eta$  are considered. Thus, a sort of delay time is predicted, during which the instantaneous moisture diffusion coefficient varies. This short period of time is followed by a pseudo-fickian

diffusion regime with a constant apparent diffusion coefficient. Comparisons with experimental results obtained on Sisal natural plant fibers can be made to show that the multiphysics model captures the actual behavior of some materials. Figure 4 displays the sorption curves of sisal fibers aged at RH = 95 %, and determined by gravimetric measurements as well as by FTIR spectroscopy. Sisal fiber exhibit a pseudo-fickian diffusive behavior, marked by a delay time at the beginning of the diffusion process. The discrepancy between the gravimetric measurements and the kinetics deduced from FTIR-spectroscopy is due to the fact that FTIR only probes the subsurface of the sample, whereas the gravimetric measurements provide a macroscopic value. Similar results, obtained during the desorption of plant fibers, have already been published in (Céline et al., 2014).

These discrepancies significantly increase with the coefficient of moisture expansion. Eventually, the coefficient of moisture absorption mainly affects both the transient and the permanent stages of the diffusion process predicted according to the multiphysics model.

## 9. Conclusions

This work is focused on developing an enhanced version of the model describing the diffusion of moisture in polymers based on the so-called thermodynamical approach first introduced by Derrien and Gilormini (2009), and then improved by Sar et al. (2012; 2013) in two papers dealing with the handling of the polymer density change as well as the differential swelling experienced by the polymer during the moisture diffusion process. For the first time, in contrast to those references, where the more simple case of thin plates was considered, the present paper is focused on treating the case of cylindrical or tubular polymer structures.

The multiphysics model presented here enables the existence of an external pressure load, whose magnitude can vary between the interior of the tube and its external surface, to be accounted for.

The expressions satisfied by the boundary conditions for the moisture have been determined for both cases in which the material is considered as subjected to either symmetrical or unsymmetrical mechanical loads.

Some preliminary results obtained through computations demonstrate that the developed model enables anomalous (i.e. non fickian) moisture uptakes to be predicted. The anomalies of diffusion mostly take place at both the very beginning of the diffusion process and the permanent regime. Non-linearities of the weight gain are thus predicted when the moisture sorption starts. After a short time, these non-linearities vanish, so that a pseudo-fickian moisture uptake follows. This pseudo-fickian regime corresponds to an instantaneous moisture diffusion coefficient independent

from the  $\frac{\sqrt{t}}{e}$  ratio. At the end of the process, the permanent regime is characterized by a maximum moisture absorption capacity, the value of which mainly depends on the magnitude of the mechanical pressure applied to the structure.

The numerical results show that the existence of a heterogeneous mechanical pressure can modify the moisture content attained in the permanent regime. In the case that the internal pressure is higher than the external pressure, the maximum moisture absorption capacity increases (in comparison with the value predicted by the symmetrical pressure load), whereas that quantity decreases when the applied internal pressure is smaller than the external pressure.



Further work will be dedicated to a thorough investigation of this new version of the model through extensive numerical tests.

Future work will focus on further enhancements, such as accounting for reversible plasticization effects experienced by the polymer during the moisture diffusion process, (i.e. the reduction of the material stiffness induced by the presence of water), and the development of tests to obtain experimental data.

## Appendix A

According to (43), the first derivative of the moisture content by the time can be obtained from the following sum:

$$\dot{C} = B_1 + B_2 \quad (\text{A-01})$$

With:

$$B_1 = D \operatorname{div} \left( \left( 1 + 3 A_0 \eta^2 k C (\operatorname{tr} \varepsilon + 1) \right) \vec{\operatorname{grad}} C - A_0 k \eta C (2 \operatorname{tr} \varepsilon - 3 \eta C + 1) \vec{\operatorname{grad}} \operatorname{tr} \varepsilon \right) \quad (\text{A-02})$$

$$B_2 = D \frac{\eta(3 A_0 k - \alpha)}{3} \operatorname{div} \left( -3 \eta C (2 \operatorname{tr} \varepsilon - 3 \eta C + 1) \vec{\operatorname{grad}} C + C (3 \operatorname{tr} \varepsilon - 6 \eta C + 1) \vec{\operatorname{grad}} \operatorname{tr} \varepsilon \right) \quad (\text{A-03})$$

Writing in cylindrical coordinates, one eventually finds the following expressions for  $B_1$  and  $B_2$ :

$$B_1 = D \left[ \left( 1 + V_1 \eta^2 C + V_2 \eta^3 C^2 \right) \left( \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right) + \eta^2 (V_1 + V_3 C) \left( \frac{\partial C}{\partial r} \right)^2 + Q_1 \lambda_1 \frac{1}{r} \frac{\partial C}{\partial r} + Q_2 \lambda_1^2 \frac{1}{r^2} C \right] \quad (\text{A-04})$$

Where:

$$\begin{cases} Q_1 = 3 A_0 \eta^2 C + 2 A_0 \eta \operatorname{tr} \varepsilon + A_0 \eta - \frac{4 \alpha \eta^2}{k} C; Q_2 = -\frac{2 A_0 \eta}{k} \\ V_1 = -3 A_0 k \operatorname{tr} \varepsilon + 2 \alpha \operatorname{tr} \varepsilon + \alpha; V_2 = 9 A_0 k - 3 \alpha; V_3 = \eta V_2 - \frac{2 \eta \alpha^2}{A_0 k} \end{cases} \quad (\text{A-05})$$

$$B_2 = D \xi \left( N_1 \frac{\partial^2 C}{\partial r^2} + (N_1 + N_2) \frac{1}{r} \frac{\partial C}{\partial r} + N_3 \left( \frac{\partial C}{\partial r} \right)^2 + 3 C \left( \frac{\lambda_1}{k} \right)^2 \frac{1}{r^2} \right) \quad (\text{A-06})$$

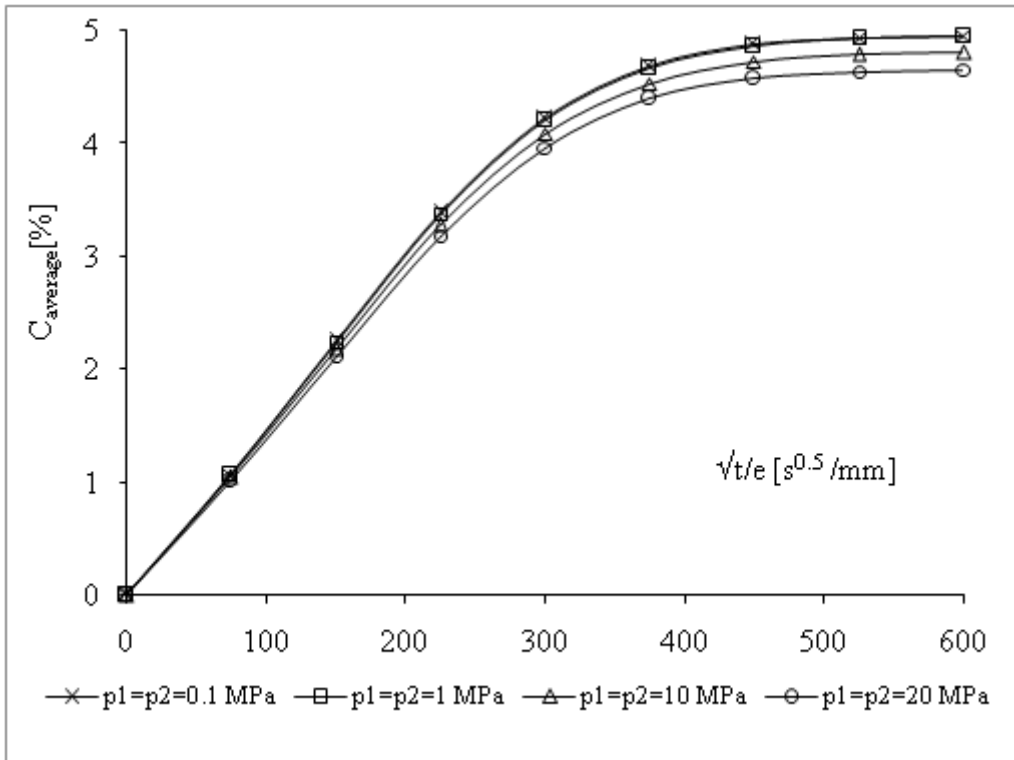
With:

$$\begin{cases} N_1 = 3 \eta C \operatorname{tr} \varepsilon - 9 \eta^2 C^2 - \frac{\alpha}{A_0 k} (3 C \eta \operatorname{tr} \varepsilon - 6 \eta^2 C^2 + C \eta) \\ N_2 = \left( -3 \operatorname{tr} \varepsilon - 1 + \frac{6 \eta \alpha}{A_0 k} C \right) \frac{\lambda_1}{k}; \xi = \frac{\eta(3 A_0 k - \alpha)}{3} \\ N_3 = 3 \eta \operatorname{tr} \varepsilon - 9 \eta^2 C - (3 \operatorname{tr} \varepsilon + 1) \frac{\alpha \eta}{A_0 k} + 3 C \eta^2 \left( \frac{\alpha}{A_0 k} \right)^2 \end{cases} \quad (\text{A-07})$$

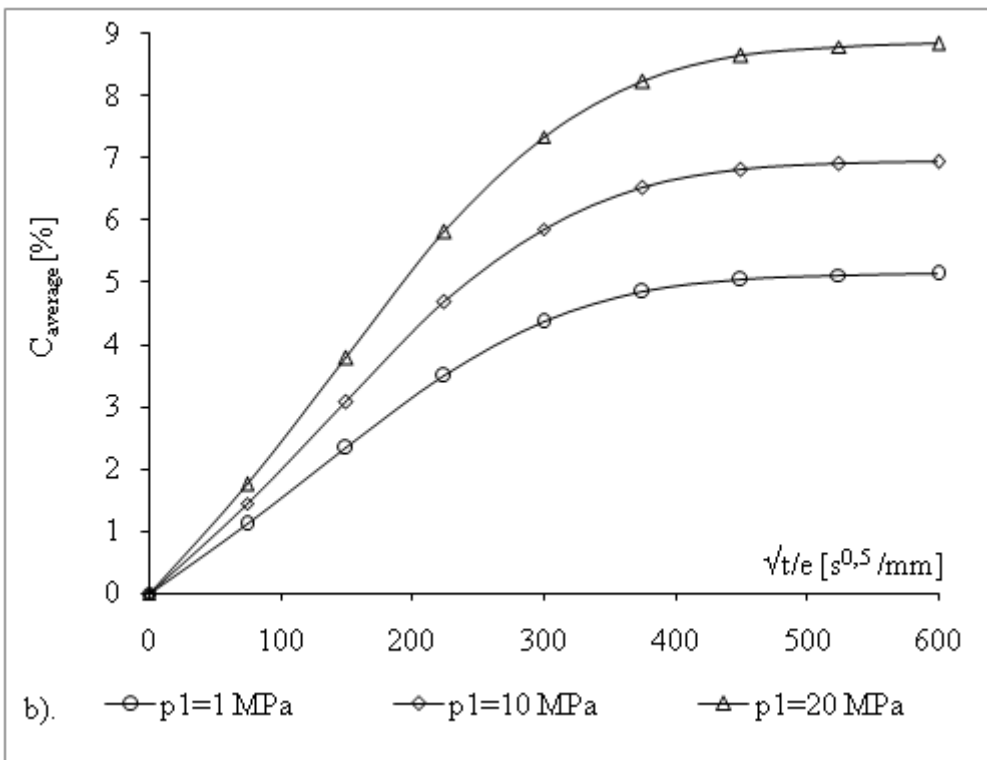
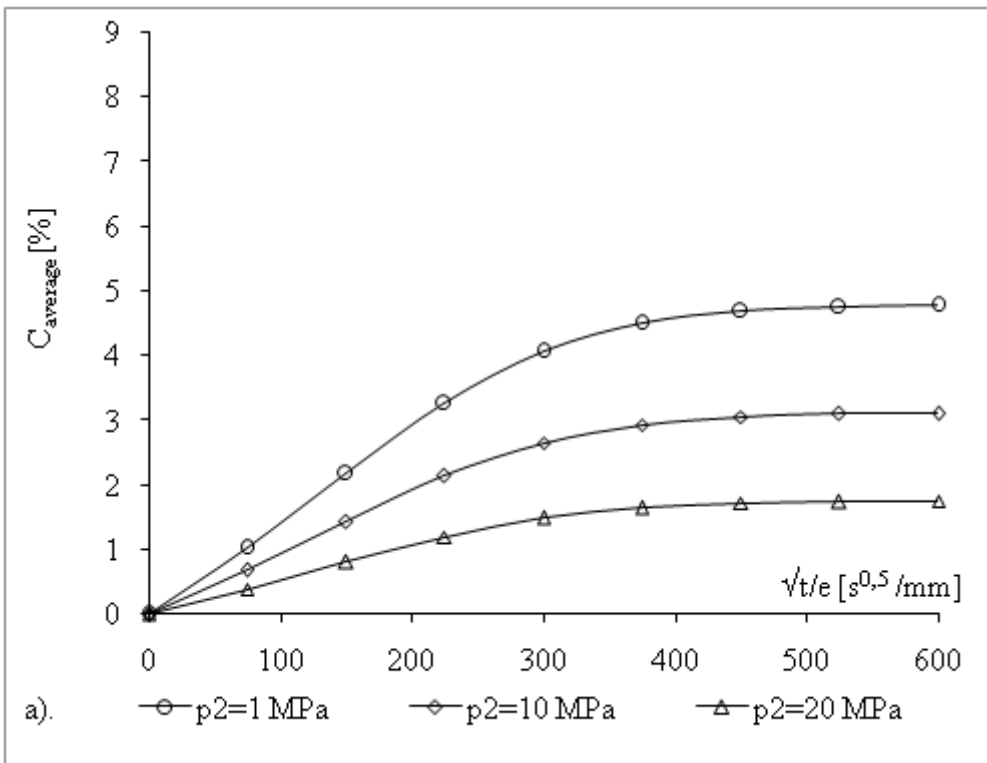
The resulting time-dependent diffusive behavior for a polymer cylinder subjected to an unsymmetrical humid ambient load is given by the sum of B<sub>1</sub> (A-04) and B<sub>2</sub> (A-06):

$$\dot{C} = D \left[ \begin{aligned} & \left( 1 + V_1 \eta^2 C + V_2 \eta^3 C^2 + \xi N_1 \right) \frac{\partial^2 C}{\partial r^2} + \left( 1 + V_1 \eta^2 C + V_2 \eta^3 C^2 + \xi (N_1 + N_2) + Q_1 \lambda_1 \right) \frac{1}{r} \frac{\partial C}{\partial r} + \\ & + \left( \eta^2 (V_1 + V_3 C) + \xi N_3 \right) \left( \frac{\partial C}{\partial r} \right)^2 + \left( \frac{3\xi}{k} + Q_2 \right) \lambda_1^2 \frac{1}{r^2} C \end{aligned} \right] \quad (\text{A-08})$$

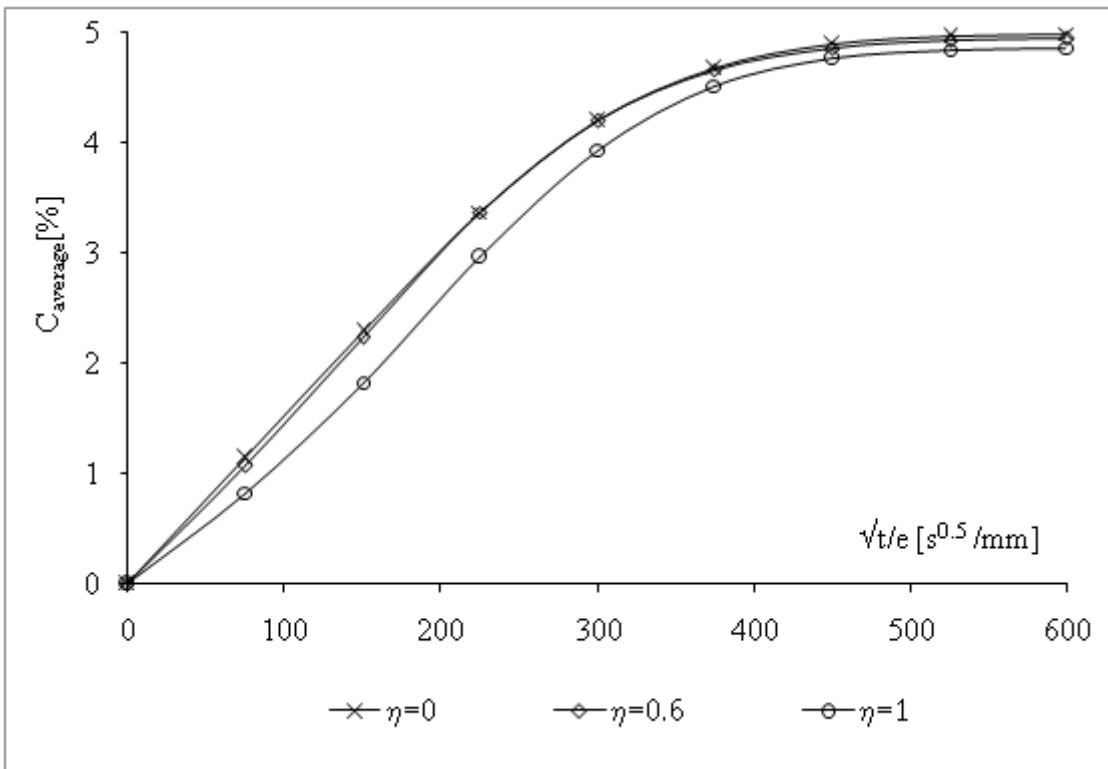
## Figures



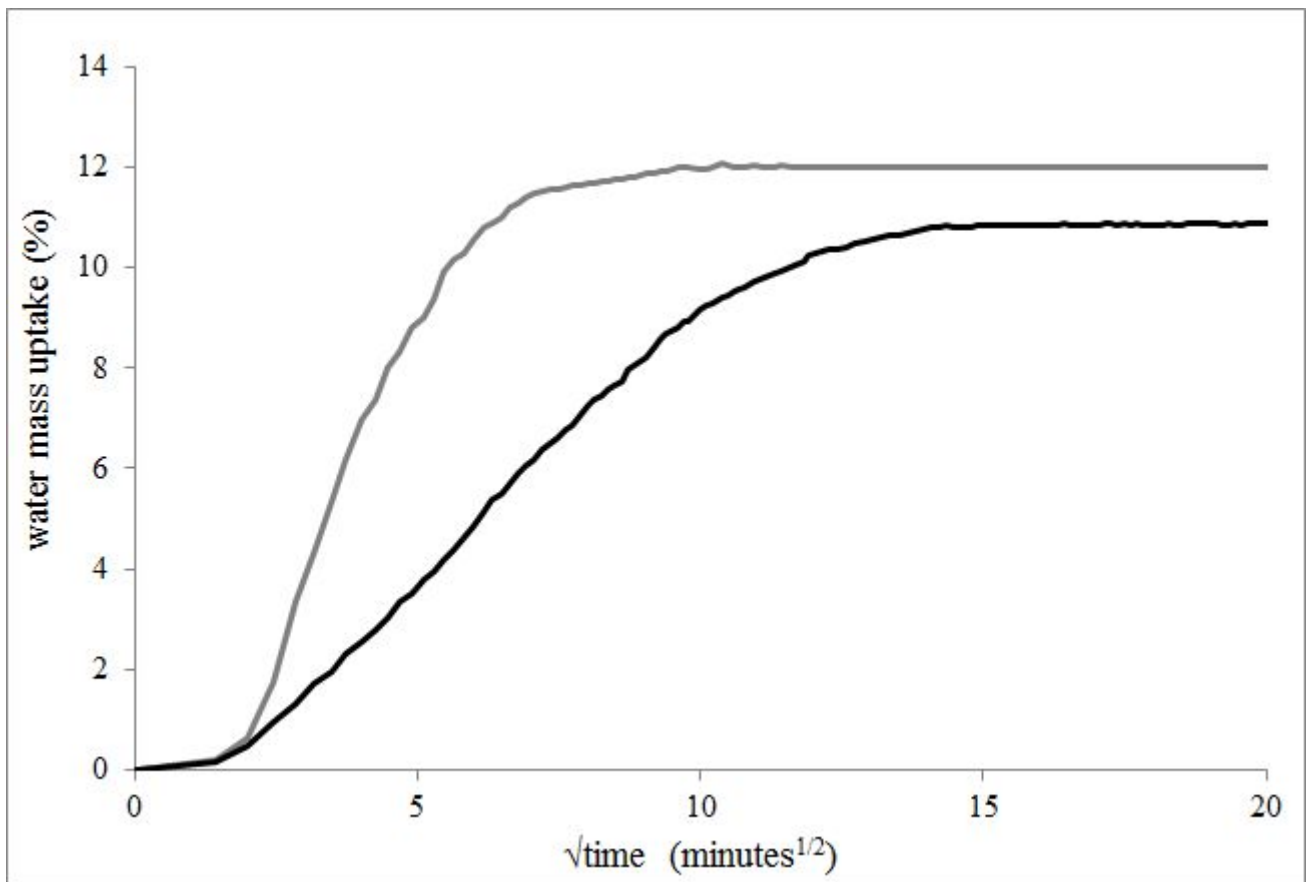
**Figure 1: Effect of a symmetrical applied pressure on the average moisture content ( $p_1 = p_2 = 0.1 ; 1, 10$  or  $20$  MPa).**



**Figure 2: Effect of an unsymmetrical applied pressure on the average moisture content a.)  $p_1 = 0.1 \text{ MPa}$ ,  $p_2 = 1, 10 \text{ or } 20 \text{ MPa}$ ; b.)  $p_2 = 0.1 \text{ MPa}$ ,  $p_1 = 1, 10 \text{ or } 20 \text{ MPa}$ .**



**Figure 3: Effect of CME on the average moisture content. Symmetrical pressure load ( $p_1 = p_2 = 1$  MPa).**



**Figure 4: Quantitative and qualitative monitoring of the water diffusion kinetic for the sisal fibre. Sorption kinetics monitored by FTIR PLS-R prediction (gray line) and gravimetric approaches (black line).**

**Table**

Input	Young's modulus (GPa)	Poisson's ratio (1)	Internal radius (mm)	External radius (mm)
Value	3	0.36	100	104

**Table 1: Input values considered for the numerical simulations.**



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