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The effect of moisture-induced swelling on the absorption capacity of transversely isotropic elastic polymer-matrix composites

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Abstract

The interaction between humid air and transversely isotropic fiber-reinforced composites with swelling polymeric matrix is considered. A model is proposed for the water saturation level in a polymer when stresses are applied, that uses directly obtainable material parameters only. In a composite, the reinforcements modify the water uptake of the polymer matrix because of the internal stresses that are induced by its restricted swelling, and this effect is evaluated. As a consequence of the coupling between stresses and absorption capacity, the sorption isotherm of a composite is ruled by the (nonlinear) Langmuir equation when the unreinforced matrix obeys the (linear) Henry's law.

Key words: Fibre reinforced composite material; Polymers; Swelling; Diffusion

1 Introduction

When a polymer is exposed to a humid environment, it absorbs some water by diffusion, and this induces swelling in frequent cases. If this polymer is the matrix of a composite, swelling cannot develop freely when the reinforcements do not absorb water, as is usually the case. As a result, internal stresses appear, which prevent the polymer matrix to absorb as much water as it would if it were free to swell. Water absorption by composites has been the subject of numerous studies with special attention focused on damage initiation

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(see, for instance, the review by Weitsman, 2000). Although many experimental observations have been carried out (like the work by Adamson, 1980, or Zimmerman *et al.*, 1984, for instance), on numerous composite systems, with several types of particles and fibers, and various polymer matrices, there does not seem to be a theory available that takes full advantage of the results provided by the micromechanics of heterogeneous media. It is the purpose of this paper to make this connection, and to address the question of how the water uptake of a composite relates to its microstructure.

Coupling between stresses and diffusion has been the subject of a very elaborate theory by Weitsman (1987), where a viscoelastic behavior at finite strain was considered. Few years later, Wu (2001) limited his work to finite strain elasticity but highlighted the role of the Eshelby stress tensor. Small strain elasticity was considered by Neogi *et al.* (1986), who used a chemical potential of the Flory-Huggins-Regner type, and by Derrien and Gilormini (2006) who insisted upon coupling-induced non-Fickian effects. Of course, viscous flow is likely to play a part during the diffusion process, as stressed by Weitsman (1990) for instance, but the present work focuses on steady state, when possible transient viscous effects have vanished and the stress-strain relation is governed by small-strain linear elasticity only. This assumes the polymer is kept far enough from its glass transition temperature, even if the latter decreases when the solvent content increases. More precisely, this study concerns steady states where concentration flux is zero everywhere, in order to avoid the additional complexity mentioned above of a non-Fickian diffusion law. All the above papers include transient diffusion and are limited to non-reinforced polymers (or, more generally, classes of homogeneous materials). The theory of stress-diffusion coupling in composites has been considered scarcely, but Aboudi and Williams (2000) did propose a complex analysis for transient regimes, whereas Derrien and Gilormini (2007) focused more simply on steady state. The present study is limited to composites with transverse isotropy, which includes many frequent cases where long fibers are used as reinforcements. In addition, the simpler case of isotropic composites, already studied by Derrien and Gilormini (2007), is also considered briefly for comparisons. Temperature is assumed uniform and constant in the material, in order to put emphasis on stress-diffusion coupling and to keep the analysis as simple as possible. Within these limits, the results can nevertheless be applied to various situations. For instance, it is shown how nonlinear sorption, departing from Henry's law, can be treated. Even if water is considered here, the analysis extends to other solvents that may induce swelling of a polymer, provided that small-strain linear elasticity still applies.

The structure of the paper is as follows. First, the effect of stresses on the water uptake of a non-reinforced polymer is studied. Then, application to internal stresses induced by swelling in composites is performed when their effective bulk modulus can be described by the Mori and Tanaka model, or

the generalized self-consistent model, or the Hashin cylinder assemblage, or the lower Hashin bound. Finally, an approximate procedure is suggested when other models apply or when external loads are present.

2   Effect of applied stresses on the water uptake in a polymer

A piece of polymer material is considered, that is homogeneous and without reinforcements. When no stress is applied, and when the polymer absorbs a concentration c of water (defined as the mass of absorbed water per unit mass of polymer), it is assumed to swell isotropically according to the linear law

$$\boldsymbol{\varepsilon}^{\mathsf{s}} = \eta \, c \, \boldsymbol{i} \,, \tag{1}$$

where $\boldsymbol{\varepsilon}^{\mathsf{s}}$ denotes the swelling strain, η the coefficient of moisture expansion, and $\boldsymbol{i}$ the second-order identity tensor. As mentioned by Weitsman (2000), such a swelling law is observed in many polymers, with values of $\eta \sim .2 - .5$. In order to remain within the limits of the small-strain assumption, systems where the water uptake c is of a few percents (which is frequently the case) are considered, so that the $\eta \, c$ product keeps small. When stresses are applied, they are related to the total strain by Hooke's law combined with (1):

$$\boldsymbol{\sigma} = k_p(c)(\operatorname{tr}\boldsymbol{\varepsilon} - 3\,\eta\,c)\,\boldsymbol{i} + 2\,G_p(c)\,\boldsymbol{e} \,, \tag{2}$$

where $\operatorname{tr}(.)$ denotes the trace of a second-order tensor, and $\boldsymbol{e}$ is the deviatoric part of the total strain $\boldsymbol{\varepsilon}$. The polymer has been assumed to be isotropically elastic in (2), with a shear modulus $G_p(c)$ and a bulk modulus $k_p(c)$, that may vary with the water concentration. The case where stresses are coupled to sorption is considered here, where c depends on $\boldsymbol{\sigma}$. More precisely, c is coupled to the hydrostatic pressure applied

$$p = -\frac{1}{3}\operatorname{tr}\boldsymbol{\sigma} = -k_p(c)\left(\frac{\Delta V}{V} - 3\,\eta\,c\right) \,, \tag{3}$$

since isotropic swelling is considered. The humid air surrounding the polymer is characterized by its partial pressure of vapor p_w that determines the water uptake for a stress-free polymer, and therefore, in the conditions considered in this paper, defining the stress-sorption coupling completely amounts to determining the $c(p_w, p)$ function.

In order to analyze stress-sorption coupling, the Helmholtz free energy is considered. For the above system made of n_p moles of polymer with a dry volume V_p, it reads as follows, when water molecules have been added and a total strain has been prescribed:

$$F(c, \boldsymbol{\varepsilon}) = F_0 + n_p \, f(c) + V_p \, W(c, \boldsymbol{\varepsilon}) \,, \tag{4}$$

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where F_0 is the free energy of the dry and stress-free polymer, $f(c)$ 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 (zero stresses), and W is the elastic energy per unit volume

$$W(c, \boldsymbol{\varepsilon}) = \frac{k_p(c)}{2}(\operatorname{tr}\boldsymbol{\varepsilon} - 3\,\eta\,c)^2 + G_p(c)\,\boldsymbol{e} : \boldsymbol{e}\,. \tag{5}$$

Note that V_p is used in (4) to compute the total elastic energy, although some volume change is induced by swelling, because of the small-strain assumption. By definition, the generalized chemical potential of water in the system is given by the partial derivative of the Helmholtz free energy with respect to the number of moles of water n_w, for a fixed total strain:

$$\widetilde{\mu}_w = \left.\frac{\partial F}{\partial n_w}\right|_{\boldsymbol{\varepsilon}} = \left.\frac{\partial F}{\partial c}\right|_{\boldsymbol{\varepsilon}}\frac{\partial c}{\partial n_w} = \frac{M_w}{n_p\,M_p}\left.\frac{\partial F}{\partial c}\right|_{\boldsymbol{\varepsilon}}\,, \tag{6}$$

where the molar masses of the polymer and of water are denoted by M_p and M_w. Therefore, (3), (4) and (5) lead to:

$$\widetilde{\mu}_w = \mu_w(c) + \frac{3\,M_w\,\eta}{\rho_p}p + \frac{M_w}{\rho_p}\left[\frac{k_p'(c)}{2}(\operatorname{tr}\boldsymbol{\varepsilon} - 3\eta c)^2 + G_p'(c)\,\boldsymbol{e} : \boldsymbol{e}\right]\,, \tag{7}$$

where $\mu_w(c) = f'(c)M_w/M_p$ is the chemical potential of water in the stress-free polymer, and $\rho_p = n_p M_p/V_p$ is the mass density of the dry polymer. In (7), where $k_p'(c)$ and $G_p'(c)$ denote the derivatives of $k_p(c)$ and $G_p(c)$, the bracketed term can be neglected if both $\frac{1}{2}\frac{k_p'}{k_p}\frac{p}{k_p}$ and $\frac{1}{6}\frac{G_p'}{G_p}\frac{\sigma_{\text{eq}}}{pG_p}$, where σ_{eq} denotes the von Mises equivalent stress, are small compared to 3η. This is the case actually, since 3η is of the order of 1, and the two expressions are of the order of one percent or less when p and σ_{eq} amount to a few megapascals, since G_p and k_p are about a few gigapascals, even if k_p' and G_p' are of the order of tens of gigapascals because a c variation of 0.01 induces variations of fractions of a gigapascal (see Zimmerman *et al.*, 1984, for experimental results on epoxy resins, for instance). Therefore, k_p and G_p can be considered as being independent from c in the sequel, and the following reduced expression of the chemical potential is used:

$$\widetilde{\mu}_w = \mu_w(c) + \frac{3\,M_w\,\eta}{\rho_p}p\,. \tag{8}$$

Similar expressions, with a chemical potential that depends linearly on the hydrostatic pressure, have been obtained previously, for instance by Weitsman (1987) and Wu (2001), but without the molar mass of water appearing explicitly. Comparable expressions have also been given for diffusion in metals (Larché and Cahn, 1973, for instance), but using a density of lattice sites that is not trivial to adapt for polymers. A closer correspondence can be found with an expression obtained by Li *et al.* (1966) for the diffusion of hydrogen

in metals, but a definite advantage of (8) is that it refers to easily obtainable material parameters only: the molar mass of the solvent M_w, the mass density of the solute ρ_p, and the moisture expansion coefficient η.

A state of thermodynamic equilibrium is obtained when the chemical potentials of water in the humid environment and in the polymer are equal. In humid air, if considered as a mixture of perfect gases, the following standard expression (Atkins and de Paula, 2006, for instance) can be used:

$$\hat{\mu}_w(p_w) = \hat{\mu}_0 + RT \ln\left(\frac{p_w}{p_0}\right) \tag{9}$$

where p_0 is a reference pressure (usually taken equal to 1 bar), and $\hat{\mu}_0$ is the corresponding potential value. The chemical potential of water in the stress-free polymer can be written similarly, provided that chemical activity $a(c)$ (as defined in Atkins and de Paula, 2006, for instance) is used:

$$\mu_w(c) = \mu_0 + RT \ln\left[\frac{a(c)}{a(c_0)}\right] \tag{10}$$

where c_0 is a reference moisture content and μ_0 the corresponding potential value. Combining (10) and (8), and equating to (9) leads to

$$\frac{a(c)}{p_w} = \frac{a(c_0)}{p_0} \exp\left(\frac{\hat{\mu}_0 - \mu_0}{RT} - \frac{3 M_w \eta\, p}{RT \rho_p}\right) \approx \frac{a(c_0)}{p_0} \exp\left(\frac{\hat{\mu}_0 - \mu_0}{RT}\right)(1 - A\,\eta\,p) \tag{11}$$

where

$$A = \frac{3 M_w}{RT \rho_p}, \tag{12}$$

if p is much smaller than $RT\rho_p/(3 M_w \eta)$. This does apply, since $RT\rho_p/(3 M_w \eta) \sim 150 - 350$ MPa at ambient temperature, for instance, using the η range mentioned above, $M_w = 18$ g/mol, and $\rho_p \sim 1.2\ 10^3$ Kg/m^3. The activity can now be expressed if the standard sorption isotherm of the polymer is defined, i.e., if the equilibrium concentration in the stress-free polymer is stated. The following, Langmuir type (Carter and Kibler, 1978), expression can be used to describe a variety of sorption isotherms for stress-free polymers:

$$c(p_w) = \frac{S\,p_w}{1 + \beta\,p_w} \qquad \text{when} \qquad p = 0 \tag{13}$$

where $\beta = 0$ leads to Henry's law, i.e., to a linear isotherm $c = S\,p_w$ (Atkins and de Paula, 2006) where S denotes solubility, $\beta > 0$ corresponds to the usual Langmuir isotherm, and $\beta < 0$ may describe upwardly concave isotherms. Using (13) to get p_w as a function of c and combining with (11) for $p = 0$ leads to the following expression of the chemical activity:

$$a(c) = \frac{a(c_0)}{p_0} \exp\left(\frac{\hat{\mu}_0 - \mu_0}{RT}\right) \frac{c}{S - \beta\,c} \tag{14}$$

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and, finally, the sorption isotherm of a stressed polymer is obtained from (11) and (14) as

$$c(p_w, p) = \frac{S \, (1 - A \, \eta \, p) \, p_w}{1 + \beta \, (1 - A \, \eta \, p) \, p_w} \,. \tag{15}$$

This is the $c(p_w, p)$ function required to define the stress-sorption coupling, for the wide class of polymers obeying (13). It may be observed that it amounts to multiplying the two parameters S and β by the same factor. In the special case of Henry's law, the coupling modifies the solubility into $S' = S(1 - A\eta p)$ and, as could be intuitively inferred, a lower (resp. higher) equilibrium concentration is obtained if the polymer is submitted to a compression (resp. a tension) in a given environment.

It may be noted that the elastic moduli are not present explicitly in (15), although it has been underlined that an elastic behavior was assumed in the derivation. Actually, the volume change $\Delta V / V$ induced by a given pressure p and by the corresponding concentration c obtained from (15) does depend on k_p through (3). Conversely, $\Delta V / V$ could be given, and the resulting c value would be computed by replacing p in (15) by its expression (3): this would lead to another, equivalent but more complex, expression of coupling, with the bulk modulus k_p being explicitly present. For instance, in the special case where no volume change is allowed, $\Delta V / V = 0$ implies that a hydrostatic pressure $p = 3 k_p \eta c$ is induced by water absorption and, if the polymer obeys Henry's law for free swelling, (15) with $\beta = 0$ leads to

$$c(p_w) = \frac{S p_w}{1 + 3 S A \, k_p \, \eta^2 p_w} \qquad \text{when} \qquad \frac{\Delta V}{V} = 0 \,. \tag{16}$$

Thus, the coupling between sorption and stresses transforms a linear isotherm for free swelling into a nonlinear isotherm of Langmuir type (13) when no volume change is allowed. It is also clear from (16) that constrained swelling lowers the absorption capacity.

In summary, equation (15) is the main result of this Section: it relates the absorption capacity c of a polymer (mass of water per unit mass of dry polymer) in a humid environment defined by the partial pressure p_w to the hydrostatic component p of the applied stresses. The constants S and β of the stress-free absorption law, that can be obtained directly from sorption tests where various ambiant humidities are prescribed, are combined with the coefficient of moisture expansion η, which can also be obtained from the same tests if both mass and volume are recorded, and by coefficient A. The latter, as defined by (12), can be deduced from the molar mass M_w of water, the density ρ_p of the polymer, and temperature T.

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3 Water uptake in a composite

From now on, the polymer considered above is the matrix of a composite that contains a volume fraction f of reinforcements that do not absorb water. Swelling cannot develop freely because moisture expansion differs in the reinforcements and in the surrounding matrix, and internal elastic stresses are induced even if the outer boundary of the composite is a free surface. These stresses will affect the water uptake because of the coupling between stresses and absorption. Of course, external loads can also be applied to the composite, that would modify the hydrostatic pressure in the polymer matrix, but this additional contribution is postponed to the last section of the paper. The hydrostatic pressure induced in the matrix may *a priori* be nonuniform and, since it is coupled to a nonuniform moisture content at equilibrium, its computation is complex. Of course, if both fields happen to be uniform in some circumstances, an analytic solution may be obtainable and a relation similar to (16) is expected, where k_p would be replaced by a smaller coefficient K (since some volume change is allowed) depending on the volume fraction of reinforcements f, with (15) recovered for $f = 0$. In these conditions, the stationary stress-diffusion coupled problem considered will to some extent be similar to a thermoeasticity problem, with moisture content replacing temperature.

Consider a composite reinforced by parallel continuous fibers, such that its effective elastic behavior is transversely isotropic. Although transversely isotropic fibers could be considered in the analysis that follows, the elastic behavior of the fibers is assumed isotropic, with a bulk modulus k_r and a shear modulus G_r, in order to get more tractable expressions. The reason for getting more involved equations when the fibers are transversely isotropic is that matrix swelling induces a longitudinal extension of the fibers that requires an additional stiffness modulus in that case. The derivations, not reported here but similar to those given below, lead to similar conclusions as for isotropic fibers about the uniformity of the hydrostatic pressure in the matrix. No external stress is applied, and let the consequences of an assumed uniform water concentration c in the matrix phase be analyzed. Since the hydrostatic pressure in the matrix is of interest here, its average value can be related to the relative volume change of the composite as follows, by extending the procedure used by Kreher (1990) for isotropic composites:

$$\Delta V/V = [(1-f)\langle \boldsymbol{\varepsilon} \rangle_p + f\langle \boldsymbol{\varepsilon} \rangle_r] : \boldsymbol{i} = (1-f)\langle \boldsymbol{s}_p : \boldsymbol{\sigma} + \eta c\, \boldsymbol{i} \rangle_p : \boldsymbol{i} + f\langle \boldsymbol{s}_r : \boldsymbol{\sigma} \rangle_r : \boldsymbol{i} \tag{17}$$

using $\langle \cdot \rangle_p$ and $\langle \cdot \rangle_r$ to denote the volume averages over the matrix and the reinforcements, respectively, where the compliance tensors are $\boldsymbol{s}_p$ and $\boldsymbol{s}_r$. Since there is no external stress, $(1-f)\langle p \rangle_p + f\langle p \rangle_r = 0$ applies and, combined with

(17), gives

$$\Delta V/V = (1 - f) \left(\frac{1}{k_r} - \frac{1}{k_p} \right) \langle p \rangle_p + 3(1 - f)\eta c . \tag{18}$$

Another expression of $\Delta V/V$ can be deduced from the relation derived by Levin (1967) for thermal expansion, which can be adapted readily to the present swelling problem and gives

$$\Delta V/V = (1 - f)\eta c \, \boldsymbol{i} : \boldsymbol{i} + \eta c \, \boldsymbol{i} : (\boldsymbol{s}_r - \boldsymbol{s}_p)^{-1} : [f \boldsymbol{s}_r + (1 - f)\boldsymbol{s}_p - \overline{\boldsymbol{s}}] : \boldsymbol{i} \tag{19}$$

where $\overline{\boldsymbol{s}}$ is the composite compliance tensor. Since the matrix and the fibers are isotropic, this relation simplifies to

$$\Delta V/V = 3(1 - f)\eta c + 3\eta c \frac{f/k_r + (1 - f)/k_p - 1/\overline{k}^{3D}}{1/k_r - 1/k_p} \tag{20}$$

where $1/\overline{k}^{3D} = \boldsymbol{i} : \overline{\boldsymbol{s}} : \boldsymbol{i}$ denotes the elastic compressibility of the composite, *i.e.*, the (anisotropic) volume change of the composite would be equal to $-p_{\text{ex}}/\overline{k}^{3D}$ if it were submitted to an (isotropic) external outer pressure p_{ex}. Finally, an expression of the average pressure in the matrix induced by a uniform water concentration c is obtained from (18) and (20):

$$\langle p \rangle_p = \frac{3\eta c}{1 - f} \frac{f/k_r + (1 - f)/k_p - 1/\overline{k}^{3D}}{(1/k_r - 1/k_p)^2} . \tag{21}$$

The fibers arrangement dictates the value of $\overline{k}^{3D}$, and (21) applies actually to any two-phase composite made of isotropic phases, be it anisotropic or isotropic.

In order to decide if the hydrostatic pressure in the matrix is uniform or not, it is necessary to compute the elastic energy $\overline{U}$ stored in the composite by the swelling process. Summing the local elastic energy in the two phases gives

$$2\overline{U} = (1 - f)\langle \boldsymbol{\sigma} : \boldsymbol{\varepsilon} - \eta c \, \boldsymbol{\sigma} : \boldsymbol{i} \rangle_p + f \langle \boldsymbol{\sigma} : \boldsymbol{\varepsilon} \rangle_r = 3(1 - f)\eta c \langle p \rangle_p \tag{22}$$

since Hill's lemma (Hill, 1963) leads to $(1 - f)\langle \boldsymbol{\sigma} : \boldsymbol{\varepsilon} \rangle_p + f \langle \boldsymbol{\sigma} : \boldsymbol{\varepsilon} \rangle_r = 0$ with no external stress applied. This lemma can also be applied by replacing $\boldsymbol{\sigma}$ by $\partial \boldsymbol{\sigma}/\partial k_p$ when a fictitious variation of the matrix bulk modulus is considered:

$$\frac{\partial \overline{U}}{\partial k_p} = (1 - f) \left\langle \left. \frac{\partial U}{\partial k_p} \right|_{\boldsymbol{\sigma}} \right\rangle_p + (1 - f) \left\langle \left. \frac{\partial U}{\partial \boldsymbol{\sigma}} \right|_{k_p} : \frac{\partial \boldsymbol{\sigma}}{\partial k_p} \right\rangle_p + f \left\langle \left. \frac{\partial U}{\partial \boldsymbol{\sigma}} \right|_{k_p} : \frac{\partial \boldsymbol{\sigma}}{\partial k_p} \right\rangle_r =$$

$$= -\frac{1 - f}{2k_p^2} \langle p^2 \rangle_p + (1 - f) \left\langle \boldsymbol{\varepsilon} : \frac{\partial \boldsymbol{\sigma}}{\partial k_p} \right\rangle_p - \eta c (1 - f) \left\langle \boldsymbol{i} : \frac{\partial \boldsymbol{\sigma}}{\partial k_p} \right\rangle_p + f \left\langle \boldsymbol{\varepsilon} : \frac{\partial \boldsymbol{\sigma}}{\partial k_p} \right\rangle_r =$$

$$= -\frac{1 - f}{2k_p^2} \langle p^2 \rangle_p + 3(1 - f)\eta c \frac{\partial \langle p \rangle_p}{\partial k_p} , \tag{23}$$

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which, combined with (22), allows to relate the average hydrostatic pressure in the matrix to the average of its square:

$$\langle p^2 \rangle_p = -3\eta \, c \, \frac{\partial \langle p \rangle_p}{\partial 1/k_p}. \tag{24}$$

This expression could alternatively be obtained by combining several results of Kreher (1990), but a direct derivation has been preferred here for clarity. Uniformity of the pressure in the matrix is equivalent to its variance $\langle (p - \langle p \rangle_p)^2 \rangle_p = \langle p^2 \rangle_p - \langle p \rangle_p^2$ being zero, which reads as follows, using (24) and (21):

$$\frac{\partial 1/\overline{k}^{3D}}{\partial 1/k_p} = \frac{1}{1-f} \left(\frac{1/\overline{k}^{3D} - 1/k_r}{1/k_p - 1/k_r} \right)^2 \tag{25}$$

for any two-phase composite with isotropic constituents, whatever its microstructure. If condition (25) is satisfied by the overall compressibility of the composite, it will develop a uniform hydrostatic pressure in the matrix if the latter is submitted to a uniform swelling, and therefore the stationary coupled problem can be solved easily.

In order to compute $\overline{k}^{3D}$, the Mori and Tanaka (1973) model is considered now, since it is widely used in the composites literature. This model predicts a transversely isotropic behavior for a composite reinforced by continuous fibers, whatever the arrangement of the fibers in the cross section. With an overbar denoting macroscopic stresses and strains, and using Hill's (1964) notations for the composite moduli, such a behavior reads

$$\begin{cases} \overline{\sigma}_{xx} = (\overline{k}^{2D} + \overline{m}) \, \overline{\varepsilon}_{xx} + (\overline{k}^{2D} - \overline{m}) \, \overline{\varepsilon}_{yy} + \overline{l} \, \overline{\varepsilon}_{zz} \\ \overline{\sigma}_{yy} = (\overline{k}^{2D} - \overline{m}) \, \overline{\varepsilon}_{xx} + (\overline{k}^{2D} + \overline{m}) \, \overline{\varepsilon}_{yy} + \overline{l} \, \overline{\varepsilon}_{zz} \\ \overline{\sigma}_{zz} = \overline{l} \, \overline{\varepsilon}_{xx} + \overline{l} \, \overline{\varepsilon}_{yy} + \overline{n} \, \overline{\varepsilon}_{zz} \end{cases} \tag{26}$$

for the components of interest here, with direction z taken parallel to the fibers. $\overline{k}^{2D}$ is the composite transverse compression modulus, *i.e.*, a lateral pressure $\overline{\sigma}_{xx} = \overline{\sigma}_{yy} = -\overline{p}$ applied in plane strain ($\overline{\varepsilon}_{zz} = 0$) induces $2\overline{\varepsilon}_{xx} = 2\overline{\varepsilon}_{yy} = -\overline{p}/\overline{k}^{2D}$, and $\overline{l}, \overline{m}, \overline{n}$ are the other composite moduli that come into play in the absence of longitudinal shear. The expression of $\overline{k}^{3D}$ can be obtained by first solving (26) with respect to the strain components:

$$\begin{cases} \overline{\varepsilon}_{xx} = \frac{1}{4\overline{m}(\overline{n}\overline{k}^{2D} - \overline{l}^2)} \{ [\overline{n}(\overline{k}^{2D} + \overline{m}) - \overline{l}^2]\overline{\sigma}_{xx} - [\overline{n}(\overline{k}^{2D} - \overline{m}) - \overline{l}^2]\overline{\sigma}_{yy} - 2\overline{l}\overline{m} \, \overline{\sigma}_{zz} \} \\ \overline{\varepsilon}_{yy} = \frac{1}{4\overline{m}(\overline{n}\overline{k}^{2D} - \overline{l}^2)} \{ -[\overline{n}(\overline{k}^{2D} - \overline{m}) - \overline{l}^2]\overline{\sigma}_{xx} + [\overline{n}(\overline{k}^{2D} + \overline{m}) - \overline{l}^2]\overline{\sigma}_{yy} - 2\overline{l}\overline{m} \, \overline{\sigma}_{zz} \} \\ \overline{\varepsilon}_{zz} = \frac{2\overline{m}}{4\overline{m}(\overline{n}\overline{k}^{2D} - \overline{l}^2)} (-\overline{l} \, \overline{\sigma}_{xx} - \overline{l} \, \overline{\sigma}_{yy} + 2\overline{k}^{2D} \, \overline{\sigma}_{zz}) \end{cases}$$

$$\tag{27}$$

and then computing $\overline{k}^{\text{3D}} = -\overline{p}/(\overline{\varepsilon}_{xx} + \overline{\varepsilon}_{yy} + \overline{\varepsilon}_{zz})$ for $\overline{\sigma}_{xx} = \overline{\sigma}_{yy} = \overline{\sigma}_{zz} = -\overline{p}$, which gives :

$$\overline{k}^{\text{3D}} = \frac{\overline{n}\,\overline{k}^{\text{2D}} - \overline{l}^2}{\overline{k}^{\text{2D}} - 2\,\overline{l} + \overline{n}} \, . \tag{28}$$

As shown by Hill (1964), $\overline{l}$ and $\overline{n}$ can be deduced from $\overline{k}^{\text{2D}}$:

$$\overline{l} = \frac{[3(k_r - k_p) - 2(G_r - G_p)]\,\overline{k}^{\text{2D}} - 3(k_r G_p - k_p G_r)}{3(k_r - k_p) + G_r - G_p} \tag{29}$$

and

$$\overline{n} = (1 - f)\left(k_p + \frac{4G_p}{3}\right) + f\left(k_r + \frac{4G_r}{3}\right) +$$

$$+ \left[\frac{3(k_r - k_p) - 2(G_r - G_p)}{3(k_r - k_p) + G_r - G_p}\right]^2 \left[\overline{k}^{\text{2D}} - (1 - f)\left(k_p + \frac{G_p}{3}\right) - f\left(k_r + \frac{G_r}{3}\right)\right], \tag{30}$$

which means that $\overline{k}^{\text{3D}}$ can be computed from $\overline{k}^{\text{2D}}$ only. For continuous fibers with a circular cross section, the Mori and Tanaka model leads to the following expression for the transverse bulk modulus (Chen *et al.*, 1992):

$$\overline{k}^{\text{2D}} = \frac{f(k_r + G_r/3)(k_p + 4G_p/3) + (1 - f)(k_p + G_p/3)(k_r + G_r/3 + G_p)}{f(k_p + 4G_p/3) + (1 - f)(k_r + G_r/3 + G_p)} \tag{31}$$

and, combining with (28), (29) and (30), it follows that

$$\overline{k}^{\text{3D}} = \frac{[(1 - f)G_p + (1/3 + f)G_r][fk_r + (1 - f)k_p] + [1 + f(G_r/G_p - 1)]k_p k_r}{(1 - f)G_p + (1/3 + f)G_r + [1 + f(G_r/G_p - 1)][(1 - f)k_r + fk_p]} \, . \tag{32}$$

It can be verified that $\overline{k}^{\text{3D}} = k$ if $k_p = k_r = k$, and that $G_p = G_r = G$ does give the exact solution obtained by Hill (1964):

$$\overline{k}^{\text{3D}} = \overline{k}^{\text{2D}} - \frac{G}{3} = \frac{4G[fk_r + (1 - f)k_p]/3 + k_p k_r}{4G/3 + (1 - f)k_r + fk_p} \, . \tag{33}$$

Moreover, longitudinal extension is prevented when the fibers tend to be rigid and, consequently, $\overline{k}^{\text{3D}}$ tends to $\overline{k}^{\text{2D}}$; this is satisfied by (32) and (31).

It can be verified readily that (32) does satisfy (25), and therefore a uniform matrix swelling induces a uniform hydrostatic pressure in the matrix of a composite that obeys the Mori and Tanaka model. It is interesting to note that (31) is also obtained from other models: the generalized self-consistent scheme (Christensen and Lo, 1979), which improves over the Mori and Tanaka model at high volume fractions of fibers, and the Hashin cylinder assemblage (Hashin, 1972). The latter model does not predict the effective transverse shear modulus $\overline{m}$, but it can be observed that the latter is not required in (28). Moreover,

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the same expression also gives the lower Hashin (1965) bound for composites where parallel continuous reinforcements of arbitrary cross-sections with random orientations about the longitudinal axis provide overall transverse isotropy in the statistical sense. Since the pressure uniformity depends only on the expression of k^{3D}, which can be deduced from k^{2D} by using (28), it can be concluded readily that the pressure is uniform in the matrix for all these models.

The value of the pressure in the matrix can be computed from (21) and (32):

$$p = 3K\eta\,c \quad \text{with} \quad K = \frac{f}{\frac{f}{k_p} + \frac{1-f}{k_r} + \frac{1+f(G_r/G_p-1)}{(1-f)G_p+(1/3+f)G_r}}. \tag{34}$$

This pressure is positive for fibers stiffer than the matrix ($G_r > G_p$ is sufficient), which is consistent with the fibers preventing the matrix from swelling freely. The fact that a uniform pressure is obtained in the polymer matrix for a given uniform water concentration leads to a uniform generalized chemical potential in the matrix, since μ_w in (8) is defined by the local concentration and hydrostatic pressure, and there remains only to fulfill the boundary condition at the matrix-air interface to obtain the complete solution to the problem considered, which validates the initial assumption of a uniform concentration in the matrix.

As explained in the previous section, the boundary condition relates through (15) the concentration and hydrostatic pressure near the interface to the partial vapor pressure in the humid air, which gives

$$c = \frac{S\,(1 - 3AK\,\eta^2\,c)\,p_w}{1 + \beta\,(1 - 3AK\,\eta^2\,c)\,p_w}. \tag{35}$$

when (34) is used to express p. The resulting second degree equation in c has a single positive solution when $\beta < 0$ and, among its two positive solutions when $\beta > 0$, only one gives $c = 0$ for $p_w = 0$ (no water uptake in dry air). In both cases, the solution reads

$$c = S\frac{1 + \chi p_w}{2\beta(\chi - \beta)p_w}\left[1 - \sqrt{1 - \frac{4\beta(\chi - \beta)p_w^2}{(1 + \chi p_w)^2}}\right] \tag{36}$$

with $\chi = \beta + 3SAK\,\eta^2$. This expression simplifies notably if the unreinforced polymer matrix obeys Henry's law, *i.e.*, if $\beta = 0$:

$$c = \frac{S\,p_w}{1 + 3SAK\eta^2\,p_w}. \tag{37}$$

As stated at the beginning of this section, (37) is similar to (16), with $K < k_p$, as can be seen from (34), and (15) is recovered if $f = 0$. In order to get the

average water concentration c_c in the composite (mass of water over mass of dry composite), which is the directly measurable quantity, (37) can be recast as follows:

$$c_c = \frac{(1 - \widetilde{f}) \, S \, p_w}{1 + 3SAK\eta^2 \, p_w} \,, \tag{38}$$

where $\widetilde{f}$ is the mass fraction of fibers in the composite, related to f by:

$$\frac{1}{\widetilde{f}} = 1 + \frac{\rho_p}{\rho_r}\left(\frac{1}{f} - 1\right) \tag{39}$$

with ρ_r denoting the mass density of the reinforcements. Therefore, if a composite is reinforced by isotropic continuous fibers with such a microstructure that its transversely isotropic effective elastic properties can be described by the Mori and Tanaka model, by the generalized self-consistent scheme, by the Hashin cylinder assemblage, or by the Hashin lower bound, its sorption isotherm (38) is of Langmuir's type albeit its swelling polymer matrix material obeys Henry's law. The composite absorbs less water than the unreinforced polymer for two reasons: because the reinforcements do not absorb water, this corresponds the $1 - \widetilde{f}$ factor in (38), and because they induce internal stresses that restrict water absorption in the matrix, this is expressed by the denominator in (38). This effect depends on the elastic properties of the matrix and reinforcements, and on the volume fraction of the latter, among other parameters.

The above results can be compared with what would be obtained for an isotropic composite. Spherical reinforcements can be considered, with either a composite sphere assemblage structure or with such microstructures that the Mori and Tanaka model or the generalized self-consistent scheme applies, but elongated reinforcements (possibly fibers) are also included provided that the distribution is statistically isotropic and that the Hashin and Shtrikman (1963) lower bound is a reasonable estimate. In all these cases, the following expression is obtained for the effective bulk modulus:

$$\overline{k}^{\text{3D}} = \frac{4G_p[fk_r + (1 - f)k_p] + 3k_pk_r}{4G_p + 3[(1 - f)k_r + fk_p]} \,, \tag{40}$$

and it can be verified easily that (40) satisfies (25). Therefore, as shown previously by Derrien and Gilormini (2007), the pressure is uniform in the matrix for these isotropic composites if the water concentration is uniform, and (38) applies with

$$K = \frac{f}{\frac{f}{k_p} + \frac{1-f}{k_r} + \frac{3}{4G_p}} \,. \tag{41}$$

Comparing with the transversely isotropic case (34), it may be noted that the reinforcement shear modulus is absent from (41): the fibers are extended by matrix swelling in the transversely isotropic case, whereas the reinforcements

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are loaded spherically in the isotropic case. Moreover, the third term in the denominator of (34) is less than $3/(4G_p)$ if $G_r > G_p$ and, consequently, the water uptake (38) is smaller in a composite with parallel continuous fibers than with the same volume fraction of isotropically distributed reinforcements, in the same humid environment. If $G_r = G_p$ the water uptake is identical for both microstructures, since (41) coincides with (34): this is because a two-phase material with a uniform shear modulus is isotropic whatever the distribution of the phases, as shown by Hill (1964).

4 Discussion

The stationary stress-sorption coupled problem could thus be solved exactly for classes of microstructures, namely the composite cylinder assemblage, the case of long fibers with a circular section if the Mori and Tanaka model or the generalized self-consistent scheme applies, and all transversely isotropic microstructures for which the Hashin lower bound gives an acceptable estimate of the effective properties. The key to the solution was the noticeable uniformity of the hydrostatic pressure induced by a uniform swelling of the matrix, but other microstructures or models may lead to more complex fields in the matrix. It can also be shown as follows that this does happen if the differential model (Boucher, 1976) is used.

This model predicts overall elastic moduli that are comparable to those given by the generalized self-consistent scheme for moderate reinforcements contents (Christensen, 1990), but it requires a system of coupled differential equations to be solved. For fiber composites, this system was given by McLaughlin (1977), and the computation of $\overline{k}^{\text{3D}}$ is coupled to $\overline{m}$ through the following pair of simple differential equations when the fibers are rigid:

$$
\begin{cases}
\dfrac{\mathrm{d}\overline{k}^{\text{3D}}}{\mathrm{d}f} = \dfrac{1}{1-f}\left(\overline{k}^{\text{3D}} + \overline{m}\right) \\[2ex]
\dfrac{\mathrm{d}\overline{m}}{\mathrm{d}f} = \dfrac{1}{1-f}\left(\overline{k}^{\text{3D}} + \overline{m}\right)\left(1 + \dfrac{\overline{k}^{\text{3D}}}{2\overline{m}}\right)^{-1}
\end{cases}
\tag{42}
$$

where the above mentioned equality $\overline{k}^{\text{3D}} = \overline{k}^{\text{2D}}$ for rigid fibers has been used. Eliminating f from the system allows to express $\overline{k}^{\text{3D}}$ with $\overline{m}$:

$$
\overline{k}^{\text{3D}} = 2\overline{m} + Q\sqrt{\overline{m}}
\tag{43}
$$

where Q is a constant, and the computation of $\overline{k}^{\text{3D}}$ consequently reduces to solving

$$
\frac{\mathrm{d}\overline{k}^{\text{3D}}}{\mathrm{d}f} = \frac{1}{1-f}\left[\overline{k}^{\text{3D}} + \frac{1}{16}\left(Q - \sqrt{8\overline{k}^{\text{3D}} + Q^2}\right)^2\right].
\tag{44}
$$

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Since (43) applies for any value of f, Q can be obtained for $f = 0$, giving $Q = (k_p - 2G_p)/\sqrt{G_p}$ and therefore $Q = 0$ if the matrix has a Poisson's ratio ν_p of $2/7$. For this special case, (44) can be integrated readily and gives

$$\overline{k}^{\text{3D}} = k_p(1 - f)^{-3/2} . \tag{45}$$

To the best of our knowledge, this analytical solution for the differential scheme applied to a composite with continuous fibers has not been given previously. It differs from the isotropic case considered by Zimmerman (1991), where rigid spheres are dispersed in a matrix with a Poisson's ratio of $1/5$ and the exponent of $1 - f$ is -2 instead of $-3/2$. In order to test if the pressure is uniform in the matrix phase, (25) requires $\partial \overline{k}^{\text{3D}}/\partial k_p$ to be computed. Taking the partial derivative of (44) with respect to k_p, then applying the $\nu_p = 2/7$ condition and using (45) leads to the following differential equation

$$\frac{\mathrm{d}}{\mathrm{d}f}\left(\frac{\partial \overline{k}^{\text{3D}}}{\partial k_p}\right) = \frac{3}{2(1 - f)}\frac{\partial \overline{k}^{\text{3D}}}{\partial k_p} - \frac{1}{2(1 - f)^{7/4}} \tag{46}$$

which gives

$$\frac{\partial \overline{k}^{\text{3D}}}{\partial k_p} = \frac{1 + 2(1 - f)^{3/4}}{3(1 - f)^{3/2}} = 1 + f + \frac{17}{16}f^2 + ... \tag{47}$$

It is readily verified that (25) can be written as $\partial \overline{k}^{\text{3D}}/\partial k_p = 1/(1 - f) = 1 + f + f^2 + ...$ for rigid fibers, and therefore differs from (47). Consequently, the pressure is not uniform in the matrix with the differential scheme, although it is with the other models mentioned in the preceding section, since (32) leads to

$$\overline{k}^{\text{3D}} = \frac{k_p + (1/3 + f)G_p}{1 - f} \tag{48}$$

when the fibers are rigid, which does satisfy (25). It may be noted that the differential model satisfies (25) when $f \ll 1$, as shown immediately by the agreement to first order between the preceding two series expansions, but not for finite f values. The reason is that the matrix modulus k_p is replaced by the current effective bulk modulus in the high-dilution expressions used incrementally by the differential model.

When external loads are applied to a composite structure, a uniform hydrostatic pressure is very unlikely to develop through the matrix phase, with a subsequent nonuniform concentration which excludes probably an analytical solution to the coupled problem. However, an approximate procedure may be proposed that retains part of the analytical result obtained in Section 3, but still requires validation by finite element simulations for instance. If the field of water concentration in the matrix of an elementary volume of the composite can be assumed smooth enough to be replaced by its average $\langle c \rangle_p$, then the field of hydrostatic pressure induced by swelling can be computed as above

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with c replaced by $\langle c \rangle_p$. Moreover, if the additional field of hydrostatic pressure induced in the polymer matrix by the stresses applied to the composite volume element can also be assumed smooth enough to be replaced by its average $\langle p_{\text{ex}} \rangle_p$ (that may be obtained from the suitable stress localization tensor in the matrix, if available), then $p + \langle p_{\text{ex}} \rangle_p$, with p computed from $\langle c \rangle_p$, is the pressure that must be used in (15) to state the equilibrium of chemical potential from a composite volume element to another, up to the interface with humid air. With these assumptions, the following approximate result is obtained readily in the composite volume element considered:

$$c_c = \frac{(1 - \widetilde{f})Sp_w}{1 + 3\,SA\,K\eta^2 p_w}(1 - A\,\eta\,\langle p_{\text{ex}} \rangle_p) \tag{49}$$

if the matrix material obeys Henry's law, with

$$K = \frac{1}{1-f}\frac{f/k_r + (1-f)/k_p - 1/\overline{k}^{3D}}{(1/k_r - 1/k_p)^2} \tag{50}$$

where $\overline{k}^{3D}$ is the bulk modulus of the composite. Of course, (38) is recovered when no stresses are applied ($\langle p_{\text{ex}} \rangle_p$=0), and (15) is obtained when stresses are applied to an unreinforced polymer volume element ($K = 0$ if $\widetilde{f} = 0$). Note that (49) can be applied to either transversely isotropic or isotropic composites, since (50) includes both cases. Moreover, (49) can be used whatever the model, including the differential scheme, that gives a reliable prediction of the elastic bulk modulus of the composite considered, since it relaxes the requirements of the analytical solution by considering an average concentration.

Finally, two practical applications of the results obtained in this paper can be mentioned. First, the prediction of the water content in the polymer matrix of a composite may be related to chemical ageing in this phase, that would lead to degradation of the composite on long time periods. Second, swelling induces stresses at the fiber-matrix interfaces that may, in addition to the effect of external applied stresses, lead to decohesions. The prediction of this damage initiation would require, in addition to the results given here, the use of a macro-to-micro model to compute the local stresses at the interfaces.

5 Conclusions

(i) A model has been presented to relate applied stresses and absorption capacity for an unreinforced swelling polymer. Based on standard thermodynamic grounds, and able to include a variety of sorption isotherms for the unstressed polymer, it depends on simple material parameters only and does confirm the intuitive trend that a compressive stress reduces the amount of water absorbed.

(ii) This model has been applied to composite materials where reinforcements do not absorb water and thus induce internal stresses. A uniform water concentration in the matrix is found to induce a uniform hydrostatic pressure when the Mori and Tanaka model, or the generalized self-consistent model, or the Hashin cylinder assemblage, or the lower Hashin bound gives a good estimate of the effective bulk modulus.

(iii) As a consequence of the coupling between internal stresses and absorption capacity, the sorption isotherm of a composite is found to be ruled by the (nonlinear) Langmuir equation when the unreinforced matrix obeys the (linear) Henry's law.

(iv) It has been shown that the uniform-pressure result does not hold for the differential scheme, although it does for the high-dilution solution that this model uses. Thus, in order to generalize our results and to include nonzero external loads applied, an approximate procedure has been proposed. It still requires validation, by comparing to numerical simulations for instance, but it leads to a simple expression.

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