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A NEW LOOK TO NON-FICKIAN DIFFUSION

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ABSTRACT: In this paper a non linear mathematical model to describe absorption phenomena in polymers is proposed. The model is established assuming that the diffusing penetrant causes a deformation which induces a viscoelastic stress responsible for a convective field. This convective field is defined to represent an opposition of the polymer to the Fickian diffusion. Several numerical examples show the effectiveness of the model.

Key words: Non-Fickian, Viscoelastic diffusion coefficient, Non linear viscoelasticity.

Mathematics Subject Classification (2000): 65M06, 65M20, 65M15

1. Introduction

In the diffusion process of a penetrant through a viscoelastic material, as for example a polymer, two main phenomena must be considered: the rate of diffusion of the fluid and the change in the internal structure of the material. If the rate of penetrant diffusion is much smaller or much bigger than the rate of relaxation of the polymer-solvent system, the transport is properly described by Fick's law. On the contrary, if the rate of penetrant diffusion is of the same order of the relaxation process, Fick's law does not represent an accurate description of the phenomenon [19, 20, 21]. The explanation lies in the fact that the diffusing penetrant causes a deformation which induces a stress that interacts with the Brownian motion of the fluid molecules. According to this explanation several authors proposed diffusion models based on a modified flux resulting from the sum of a Fickian flux J_F and a non Fickian flux J_{NF}, that is

$$\frac{\partial C}{\partial t} = -div(J_F(C) + J_{NF}(\sigma)) \ , \qquad (1)$$

where C stands for the concentration of the penetrant, $J_F(C) = -(D(C)\nabla C)$, $J_{NF}(\sigma) = -(D_v(C)\nabla\sigma)$ and σ represents the stress.The functions $D(C)$and $D_v(C)$ represent respectively the Fickian diffusion coefficient and the so called viscoelastic diffusion coefficient. Equation (1) is used for example

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in [2, 3, 6, 7, 8, 12, 14, 17] just to name a few. It is coupled with an evolution equation for the stress which introduces in the problem the strain ϵ as a third variable. In the previous works a constitutive relationship of type [1]

$$\frac{\partial \sigma}{\partial t} + \beta\sigma = \alpha\epsilon + \gamma\frac{\partial \epsilon}{\partial t}\ , \tag{2}$$

has been considered. The parameters α and γ are assumed to be constant and the parameter β, which represents the inverse of the relaxation time, is considered constant in [16, 17] and in [3, 7, 8] concentration dependent.

One of our main concerns in this paper is to properly understand the meaning of the non-Fickian flux J_{NF}. In [16, 17] the authors consider that the stress related to the viscoelastic behavior of the material leads to a negative convex flux, consequently considering that the strain in (2) is linearly related with the penetrant concentration $\epsilon = \eta C$, a model of type

$$\frac{\partial C}{\partial t} = D\Delta C + D_v\eta\gamma C_{xx} + D_v\eta(\alpha - \gamma\beta)\int_0^t e^{\beta(s-t)}C_{xx}(x,s)ds \tag{3}$$

is proposed in [16], where D and D_v are assumed constant, and Dv is considered negative.

An analogous model has been studied in [9] while describing the permeation of a fluid trough a membrane. The authors established that when $D_v < 0$ the steady flux accounts for the existence of a convective negative flux related to the viscoelastic properties of the membrane. Also analogous models where used in [3, 6, 7]. However in these works the viscoelastic behavior is not considered responsible for a negative convective flux and consequently D_v is assumed positive.

As a result of the previous arguments it seems that different interpretations exist in the literature concerning the meaning of J_{NF} and its mathematical description. In this paper we present a mathematical deduction of J_{NF} that incorporates parameters which can be obtained from rheological experiments. The following aspects will be addressed:

(i) To account for a typical response to a strain ϵ several relaxation times will be introduced using Boltzman type integrals relating σ and C;
(ii) Two different approaches to obtain functional relations for the stress driven diffusion coefficient D_v in function of C will be established;
(iii) A non linear functional relation between ϵ and C will be presented;
(iv) Linear functional relations for the Young modulus in function of C will be established.

In Section 2 the model is established. In Section 2.1 a generalized Maxwell-Wiechert model is presented. In Section 2.2 functional relations for D_v are introduced following two different approaches. A non linear expression for the strain is deduced in Section 2.3. A linear relation between the Young modulus of the spring elements associated to the generalized Maxwell-Wiechert model and C is introduced in Section 2.4. The complete non linear model is established in Section 2.5. In Section 3 several numerical experiments are exhibited, evidencing a sound physical behavior. Finally in Section 4 some closing remarks are presented.

2. Mathematical model

2.1. Preliminary considerations. Let us consider a polymeric sample $\Omega \subset \mathbb{R}^3$ initially void, with boundary $\partial\Omega = \Gamma^{in} \cup \Gamma^{out}$.

We model in what follows the sorption by Ω of a penetrant solvent. The solvent of concentration C penetrates the matrix at Γ^{in}, diffuses through the device and at Γ^{out} the solvent flux is zero (impermeable wall condition). From (1) we have

$$\frac{\partial C}{\partial t} = \nabla \cdot (D(C)\nabla C) + \nabla \cdot (D_v(C)\nabla \sigma) \quad \text{in} \quad \Omega \times (0, T] \ . \tag{4}$$

To define the stress σ we use a Maxwell-Wiechert model [1, 18] with $n+1$ arms in parallel, where n of them are Maxwell fluid elements and one of them is a free spring as in figure 1. When the solvent penetrates the polymeric sample Ω a strain occurs and the corresponding stress is then given by

$$\sigma(t) = -E_0(C)\epsilon - \sum_{i=1}^{n} E_i(C) \int_0^t e^{-\frac{1}{\mu_i}\int_s^t E_i(C(r))dr} \frac{\partial \epsilon}{\partial s}(s) ds \ . \tag{5}$$

where $E_i(C)$, for $i = 1, 2, ..., n$, are the Young modulus of the spring elements associated to each of the n Maxwell fluid arms, μ_i, for $i = 1, 2, .., n$, represents the viscosity and $E_0(C)$ stands for the Young modulus of the free spring. Equation (5) is the solution of the constitutive equation of the Maxwell-Wiechert model assuming that $\sigma(0) = 0$ and that the Young modulus of the spring elements are concentration dependent. We note that in (5) the strain ϵ caused by the penetrant induces a viscoelastic stress response with opposite sign.

Implicitly, (5) assumes that the viscoelastic behavior of the material (penetrant plus polymer) can be properly described by a linear viscoelastic model.

Indeed, only in this hypothesis the total, local, stress in the material can be computed as the sum of the stresses competing to each Maxwell-Wiechert arm (see (5)). Physically speaking, this implies that the chosen relation between stress and deformation works for not so important deformations that slowly develop in time. This is also the reason why fixed boundary conditions have been considered in the model presented in this paper.

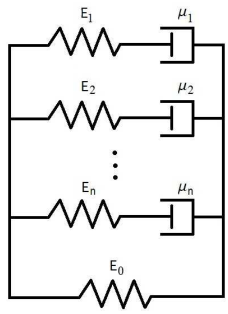

FIGURE 1. Maxwell-Wiechert model

Replacing (5) in (4) we have

$$\begin{aligned} \frac{\partial C}{\partial t} &= \nabla \cdot (D(C)\nabla C - D_v(C)\nabla \cdot (E_0(C)\epsilon)) \\ &\quad -\nabla \cdot \left(D_v(C)\nabla \cdot \left(\sum_{i=1}^{n} E_i(C) \int_0^t e^{\alpha_i(s)} \frac{\partial \epsilon}{\partial s}(s) ds \right) \right) \ , \end{aligned} \tag{6}$$

where $\alpha_i(s) = -\frac{1}{\mu_i}\int_s^t E_i(C(r))dr$, for all $i = 1, 2, .., n$.

Equation (6) is completed with the initial condition

$$C(x, 0) = C_0, \ x \in \Omega \ , \tag{7}$$

and the boundary conditions

$$C = C_{in} \text{ on } \mathrm{int}(\Gamma^{in}) \times (0, T] \ , \tag{8}$$

$$J(C) \cdot \eta = 0 \text{ on } \mathrm{int}(\Gamma^{out}) \times (0, T] \ , \tag{9}$$

where η represents the unit outer normal and the flux J is defined by

$$\begin{aligned} J(C) &= -D(C)\nabla C + D_v(C)\nabla \cdot \left(\sum_{i=1}^{n} E_i(C) \int_0^t e^{\alpha_i(s)} \frac{\partial \epsilon}{\partial s}(s) ds \right) \\ &\quad + D_v(C)\nabla \cdot (E_0(C)\epsilon) \ . \end{aligned} \tag{10}$$

Conditions (8) and (9) represent a source of constant concentration at Γ^{in} and an impermeable wall at Γ^{out} respectively.

A Fujita-type [11] exponential dependence for $D(C)$ is assumed with

$$D(C) = D_{eq} exp(-\kappa(1 - \frac{C}{C_{in}})) \ , \tag{11}$$

where D_{eq} is the diffusion coefficient of the liquid agent in the fully swollen sample.

In equation (6) several concentration dependent parameters are considered. The functional relations that characterize this dependence will be established in what follows.

2.2. The viscoelastic diffusion coefficient D_v. In (6) whereas the diffusion coefficient has a well known physical meaning the viscoelastic diffusion coefficient $D_v(C)$ has not been clearly studied so far. In fact even its sign is not clear in the literature. As mentioned in Section 1 some authors [9, 16, 17] consider D_v constant and negative while in the works [2, 3, 6, 7, 8, 12] D_v is considered to be a positive parameter. In what follows we analyze the meaning of D_v and we establish concentration dependent expressions for D_v.

As we assume the existence of a stress gradient $\nabla\sigma$, this implies the existence of a velocity field ν. Then the non-Fickian flux J_{NF} can be interpreted as a convective field of form

$$J_{NF} = \nu C \ . \tag{12}$$

We present in what follows two different approaches to compute D_v. The first one is based on Darcy's law and the second one on the Hagen-Poiseuille equation.

Let us consider that the polymeric sample is a porous media. Then by Darcy's law [22] we have

$$\nu = -K\nabla p \ , \tag{13}$$

where p is the hydrostatic pressure and K is the hydraulic conductivity. The parameter K can be computed using the Kozeny-Carman equation

$$K = \frac{r_f^2 \alpha^3}{4G\mu(1-\alpha)^2} \ , \tag{14}$$

where r_f is the fiber radius, α is the concentration dependent porosity, μ is the pure solvent shear viscosity and G is the Kozeny constant. The porosity α is defined by $\alpha = C/\rho_S$ where ρ_S represents the pure penetrant density. Theoretical work [22] indicates that the Kozeny constant G develops a steep gradient. In fact it slowly increases from 5 to 7 in the range $0 < \alpha \leq 0.82$ and, then, rapidly grows up to 49 for $\alpha = 0.99$.

As the convective field is induced by the stress we have

$$-D_v(C)\nabla\sigma = \nu C \ ,$$

and by identifying the stress σ with the pressure p we conclude that

$$D_v(C) = KC \ . \tag{15}$$

We present now a second functional relation for $D_v(C)$. The main difference of this approach is that the velocity is now computed using the Hagen-Poiseuille equation. We have

$$\nu = -\frac{R^2}{8\mu}\nabla p \ , \tag{16}$$

where R stands for the radius of a virtual cross section of the polymeric sample available for the convective flux, p is the pressure drop and μ represents the viscosity of a polymer-solvent solution characterized by a polymer concentration equal to C (local solvent concentration). Thus from (12), (16) and identifying again the pressure p with the viscoelastic stress σ we conclude that

$$D_v(C) = \frac{R^2 C}{8\mu} \ . \tag{17}$$

Let us study now the evolution in time of R. Let m_S and V_S represent the mass and volume of the solvent respectively. If ρ_S represents its density then $m_S = \rho_S V_S$ and $C = \frac{m_S}{V_0+V_S}$, where V_0 is the volume of the polymeric matrix in the dry state. We conclude then

$$V_s = \frac{C}{\rho_S - C} V_0 \ ,$$

and as $V_0 = \Delta x_0 S$, we have

$$\frac{V_S}{\Delta x_0} = \frac{C}{\rho_S - C} S \ . \tag{18}$$

The first member in (18) can be interpreted as a virtual cross section S_v available for convective flow. As $S_v = \pi R^2$ and $S = \pi R_0^2$ where R_0 is the radius of the dry sample, we deduce

$$R^2 = \frac{C}{\rho_S - C} R_0^2 \ . \tag{19}$$

From (17) and (19) we finally have

$$D_v(C) = \frac{C^2}{\rho_S - C} \frac{R_0^2}{8\mu} \ . \tag{20}$$

We note that from both approaches, (15) and (20), we can conclude that:

- $D_v(C)$ is positive, thus the non-Fickian flux J_{NF} represents a contribution to the mass flux which develops from high stress to low stress.
- $D_v(C)$ is an increasing function of C.
- $D_v(0) = 0$ which accounts for the fact that no stress gradient contributes to the mass flux when $C = 0$.

Although the Darcy approach takes its origin from the study of fluid motion in a porous medium while the Hagen-Poiseuille approach is strictly connected to the flux of an homogeneous fluid, both of them lead to qualitatively similar behaviors for the Dv dependence on local solvent concentration C (Figure 2). The shear viscosity considered is that of the pure solvent (0.001 Pas for water) in the Darcy case and that of the polymer-solvent system (10^5 Pas) in the Hagen-Poiseuille case. The plots in Figure 2 evidence that the Darcy approach leads to smaller values for Dv which reflects a smaller importance of the polymer-solvent viscoelastic properties on penetrant uptake. In the simulation of D_v, computed from the Hagen-Poiseuille approach, we considered $R_0 = 0.005$ m.

2.3. Relation between deformation and local solvent concentration. In order to relate the strain ϵ and the concentration C let us consider, for a sake of simplicity, a cylindrical dry polymeric sample with cross section S and volume V_0 in the dry state. We assume that the deformation ϵ occurs only

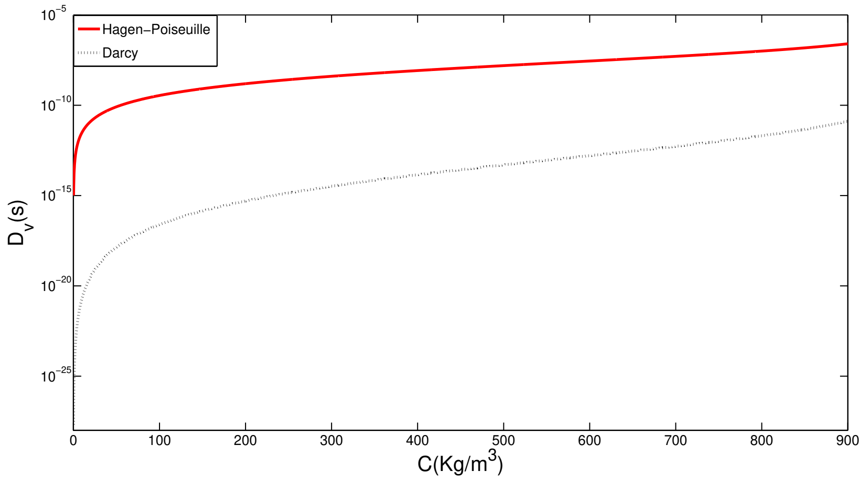

FIGURE 2. Quantitative comparison of the two approaches for D_v

in a direction orthogonal to S. If its thickness in the dry state is represented by Δx_0 then

$$\Delta x_0 = \frac{V_0}{S} \, .$$

After swelling the thickness of the sample can be defined as

$$\Delta x = \frac{V_0 + V_S}{S} \, ,$$

where V_S is the volume of solvent absorbed by the sample up to time t. As

$$\epsilon = \frac{\Delta x - \Delta x_0}{\Delta x_0} \, ,$$

we have

$$\epsilon = \frac{\frac{V_0+V_S}{S} - \frac{V_0}{S}}{\frac{V_0}{S}} \, ,$$

which leads to

$$\epsilon = \frac{V_S}{V_0} \, .$$

Let m_S and ρ_S represent the solvent mass and density respectively. We use the fact that $V_S = \dfrac{m_S}{\rho_S}$, to obtain

$$\epsilon = \frac{m_S}{\rho_S V_0} \, . \qquad (21)$$

We note that equation (21) holds under the reasonable hypothesis that the mixing of the polymer and the solvent occurs in an ideal manner that is the final volume of the swelling element is $V_0 + V_S$. Considering that the concentration C is defined by $C = \dfrac{m_S}{V_0 + V_S}$, then from (21) we easily deduce that $\epsilon = f(C)$ with

$$f(C) = \frac{C}{\rho_S - C} \ . \tag{22}$$

From (6) after integrating by parts we obtain

$$\begin{aligned}
\frac{\partial C}{\partial t} \ &= \ \nabla \cdot \Bigg(D(C)\nabla C - D_v(C)\nabla \cdot (\sum_{i=0}^{n} E_i(C) f(C)) \\
&\quad + f(0) \sum_{i=1}^{n} E_i(C) e^{-\frac{1}{\mu_i}\int_0^t E_i(C(r))dr} \Bigg) \\
&\quad + \nabla \cdot \left(D_v(C)\nabla \cdot \left(\sum_{i=1}^{n} \frac{E_i(C)}{\mu_i} \int_0^t E_i(C(s)) e^{\alpha_i(s)} f(C(s)) ds \right)\right) \ .
\end{aligned} \tag{23}$$

2.4. Behavior of Young modulus. We begin by assuming that we have a purely elastic material with initial Young modulus E^0, which represents the Young modulus of the sample in the dry estate. The bounds that link polymer chains, known as cross-links, have a significant role in the mechanical properties of materials. Let us define the cross-link density in the dry estate of the sample as

$$\rho_x^0 = \frac{\xi^0}{V_0} \ , \tag{24}$$

where ξ^0 represents the number of moles of cross-links per unit of volume in the dry estate. In the swollen state the cross-link density becomes

$$\rho_x = \frac{\xi^0}{V_0 + V_S} \ , \tag{25}$$

and thus we have from (24) and (25)

$$\frac{\rho_x}{\rho_x^0} = \frac{V_0}{V_0 + V_S} \ . \tag{26}$$

As $C = \frac{m_S}{V_0+V_S}$ and $\rho = \frac{m_S}{V_S}$ we deduce from (26)

$$\frac{\rho_x}{\rho_x^0} = \frac{\rho_S - C}{\rho_S} \ . \tag{27}$$

As the Young modulus of a polymer is related to the cross-link density by $E = 3\rho_x RT$ [13] where R is the universal gas constant and T is the absolute temperature, then $\frac{\rho_x}{\rho_x^0} = \frac{E}{E^0}$. Therefore we conclude from (27) that

$$E(C) = E^0 \frac{\rho_S - C}{\rho_S} \ . \tag{28}$$

Equation (28) holds for purely elastic materials. In the case of viscoelastic materials we will assume that the elastic contributions in each Maxwell arm satisfy (28).

2.5. Complete non linear model. Let E_i^{ini} for $i = 0, 1, 2, ..., n$ denote the Young modulus of each spring element in the dry state. Taking into consideration (28) for each Maxwell arm and the free spring, after integrating by parts we rewrite (23) as

$$\begin{aligned}\frac{\partial C}{\partial t} \ &= \ \nabla \cdot \Bigg(D(C)\nabla C - \frac{D_v(C)}{\rho_S}\left(\sum_{i=0}^{n} E_i^{ini}\right)\nabla C \\ &\quad + \frac{f(0)D_v(C)}{\rho_S}\sum_{i=1}^{n} E_i^{ini}\nabla \cdot \left(\left(\rho_S - C\right)e^{\alpha_i(0)}\right)\Bigg) \\ &\quad + \nabla \cdot \left(\frac{D_v(C)}{\rho_S^2}\nabla \cdot \left(\sum_{i=1}^{n}\frac{(E_i^{ini})^2}{\mu_i}(\rho_S - C)\int_0^t e^{\alpha_i(s)}C(s)ds\right)\right) \ ,\end{aligned} \tag{29}$$

where $D(C)$, $f(C)$ and $D_v(C)$ are given by (11), (22) and (15) respectively.

The complete non linear model (CNLM) is given by equation (29), initial condition (7) and boundary conditions (8),(9). The flux J is given by

$$
\begin{aligned}
J(C) &= -D(C)\nabla C + \frac{D_v(C)}{\rho_S}\left(\sum_{i=0}^{n} E_i^{ini}\right)\nabla C \\
&\quad -\frac{f(0)D_v(C)}{\rho_S}\sum_{i=1}^{n} E_i^{ini}\nabla\cdot\Big((\rho_S - C)\, e^{\alpha_i(0)}\Big) \\
&\quad -\frac{D_v(C)}{\rho_S^2}\nabla\cdot\left(\sum_{i=1}^{n}\frac{(E_i^{ini})^2}{\mu_i}(\rho_S - C)\int_0^t e^{\alpha_i(s)}C(s)ds\right) \; .
\end{aligned} \tag{30}
$$

3. Numerical Results

In order to have a better understanding of the influence of the parameters in the model, we will recast CNLM in dimensionless form. Let us consider the one-dimensional case where $\Omega = [0, b]$. Then we define

$$
\begin{aligned}
C^+ &= \frac{C}{C_{in}}, \quad x^+ = \frac{x}{b}, \quad t^+ = \frac{tD_{eq}}{b^2}, \quad \rho_S^+ = \frac{\rho_S}{C_{in}}, \quad f^+(C^+) = \frac{C^+}{\rho_S^+ - C^+}, \\
\alpha_i^+(s) &= -\frac{1}{D_{e_i}\rho_S^+}\int_s^{t^+}(\rho_S^+ - C^+(r))dr, \quad D^+(C^+) = exp(-\beta(1 - C^+)) \; .
\end{aligned}
$$

The diffusion coefficient D_v from Darcy's law (15) and Hagen-Poiseuille (20) are defined by

$$
D_v^+(C^+) = \frac{K}{D_{eq}}C^+ \; , \tag{31}
$$

$$
D_v^+(C^+) = \frac{(C^+)^2}{(\rho_S^+ - C^+)8\sum_{i=1}^{n} E_i^{ini} D_{e_i}} \; , \tag{32}
$$

respectively. The Deborah numbers D_{e_i} are defined as

$$
D_{e_i} = \frac{\tau_i D_{eq}}{b^2} \; ,
$$

with $\tau_i = \frac{\mu_i}{E_i^{ini}}$ for all $i = 1, 2, ..., n$.

We rewrite CNLM in dimensionless form as

$$\begin{aligned}\frac{\partial C^+}{\partial t^+} &= \nabla\cdot\Bigg(D^+(C^+)\nabla C^+ - \frac{D_v^+(C^+)}{\rho_S^+}\left(\sum_{i=0}^n E_i^{ini}\right)\nabla C^+ \\ &\quad + \frac{f^+(0)D_v^+(C^+)}{\rho_S^+}\sum_{i=1}^n E_i^{ini}\nabla\cdot\left(\left(\rho_S^+ - C^+\right)e^{\alpha_i^+(0)}\right)\Bigg) \\ &\quad + \nabla\cdot\left(\frac{D_v^+(C^+)}{(\rho_S^+)^2}\nabla\cdot\left(\sum_{i=1}^n \frac{(E_i^{ini})}{De_i}(\rho_S^+ - C^+)\int_0^{t^+} e^{\alpha_i^+(s)}C^+(s)ds\right)\right) ,\end{aligned} \tag{33}$$

with the initial condition

$$C^+(x^+,0) = C_0/C_{in},\ x^+\in[0,1] , \tag{34}$$

and the boundary conditions

$$C^+(1,t^+) = 1 \text{ in } (0,T^+] , \tag{35}$$

$$J^+(C^+(0,t^+)) = 0 \text{ in } (0,T^+] , \tag{36}$$

where

$$\begin{aligned}J^+(C^+) &= -D^+(C^+)\nabla C^+ + \frac{D_v^+(C^+)}{\rho_S^+}\left(\sum_{i=0}^n E_i^{ini}\right)\nabla C^+ \\ &\quad - \frac{f^+(0)D_v^+(C^+)}{\rho_S^+}\sum_{i=1}^n E_i^{ini}\nabla\cdot\left(\left(\rho_S^+ - C^+\right)e^{\alpha_i^+(0)}\right) \\ &\quad - \frac{D_v^+(C^+)}{(\rho_S^+)^2}\nabla\cdot\left(\sum_{i=1}^n \frac{(E_i^{ini})}{De_i}(\rho_S^+ - C^+)\int_0^{t^+} e^{\alpha_i^+(s)}C^+(s)ds\right) ,\end{aligned} \tag{37}$$

In what follows we fix $n = 1$, that is we consider one Maxwell fluid element in parallel with a free spring. We consider the following values for the parameters and initial conditions $\rho_S = 1000\ kg/m^3$, $C_0 = 20\ Kg/m^3$, $C_{in} = 350\ Kg/m^3$, $r_f = 2\times10^{-9}\ m$, $G = 5$, $\kappa = 0.5$ and $D_{eq} = 3,74\times10^{-9}\ m^2/s$. The porosity α is given by $\alpha = \frac{C}{\rho_S}$. We define M_{t^+} as the total mass inside the matrix at time t^+ as

$$M_{t^+} = \int_0^1 C^+(x,t^+)dx .$$

In Figure 3 we plotted the non-Fickian part of the flux J_{NF}, considering the definition of D_v established from Darcy's law (31) and the definition of D_v deduced from Hagen-Poiseuille equation (32) respectively, with $D_{e_1} = 0.1$, $E_0^{ini} = 1 \times 10^5\ Pa$ and $E_1^{ini} = 2 \times 10^5\ Pa$. When D_v is given by (32), since J_{NF} is negative, a higher opposition to the diffusion is observed, in agrement with what we observed in Figure 2. In Figure 4 we plotted a comparison of the complete flux J when Dv is given by (31) and (32) respectively. In accordance with the behavior observed in Figure 3 when D_v is given by (32) the model predicts a slower sorption of the solvent into the polymeric sample.

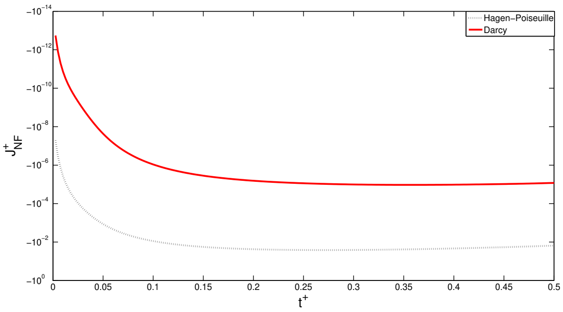

FIGURE 3. Non-Fickian flux J_{NF} for $x^+ = 0.5$

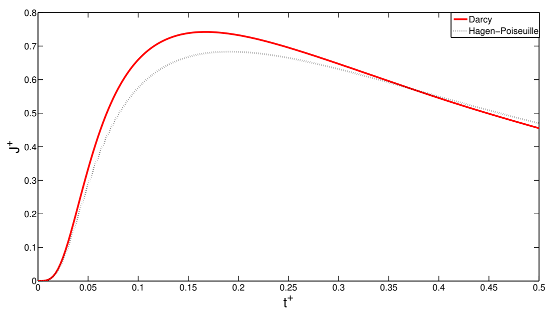

FIGURE 4. Total flux J^+ for $x^+ = 0.5$

In Figures 5 and 6 we exhibit plots of J^+ as a function of D_{e_1} with Dv as in (31) and (32) respectively. In the case of Figure 5 we observe an accurate physical behavior since as expected J^+ is a decreasing function of D_{e_1}. In Figure 6 we observe that J^+ is not a monotone function of D_{e_1}.

In Figures 7 and 8 we plotted M_{t^+} as a function of E_0^{ini} with Dv given by (31) and (32) respectively. In both cases we observe that M_{t^+} is a decreasing

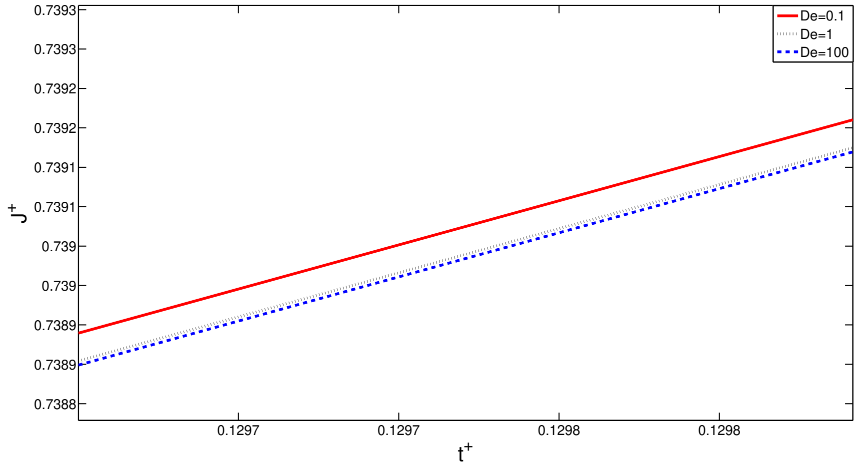

FIGURE 5. J^+ for $x^+ = 0.5$ as a function of D_{e_1} with D_v deduced from Darcy's law (31), $E_0^{ini} = 1 \times 10^5\ Pa$ and $E_1^{ini} = 2 \times 10^5\ Pa$

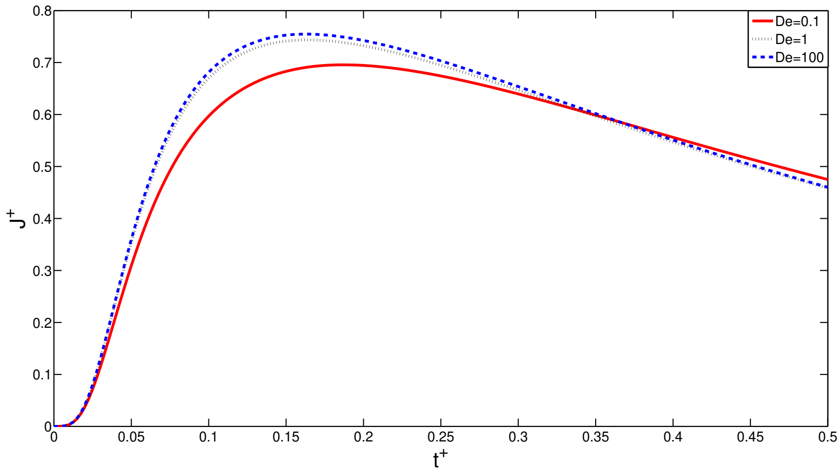

FIGURE 6. J^+ for $x^+ = 0.5$ as a function of D_{e_1} with D_v deduced from Hagen-Poiseuille equation (32), $E_0^{ini} = 1 \times 10^5\ Pa$ and $E_1^{ini} = 2 \times 10^5\ Pa$

function of E_0^{ini}. This is a physically sound behavior since as E_0 increases the solvent will encounter more resistance to diffuse into the polymer.

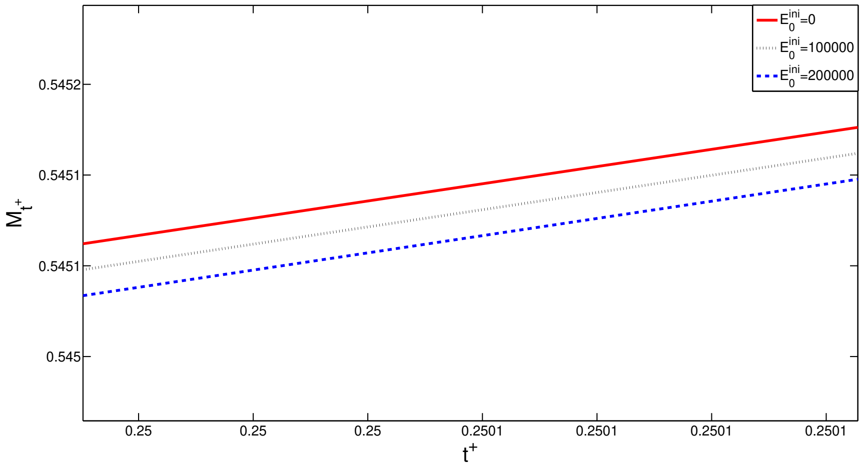

FIGURE 7. M_{t^+} as a function of E_0^{ini} with D_v given by (31), $E_1^{ini} = 2 \times 10^5\ Pa$ and $D_{e_1} = 1$

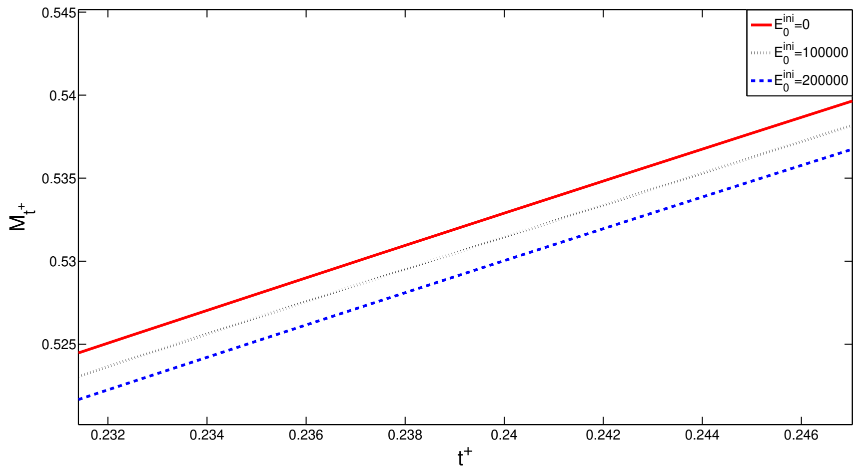

FIGURE 8. M_{t^+} as a function of E_0^{ini} with D_v given by (32), $E_1^{ini} = 2 \times 10^5\ Pa$ and $D_{e_1} = 1$

If we consider that the elastic contributions E_i are constant, for $i = 0, 1, ..., n$, then from (6) we get

$$\begin{aligned} \frac{\partial C^+}{\partial t^+} &= \nabla \cdot \left(D^+(C^+)\nabla C^+ - D_v^+(C^+)\left(\sum_{i=0}^{n} E_i\right)\nabla\left(\frac{C^+}{\rho_S^+ - C^+}\right)\right. \\ &\quad + \nabla \cdot \left(D_v^+(C^+)\nabla \cdot \left(\sum_{i=1}^{n} \frac{(E_i^{ini})}{De_i}\int_0^{t^+} e^{-\frac{s-t}{De_i}}\frac{C^+(s)}{\rho_S^+ - C^+(s)}ds\right)\right), \end{aligned} \tag{38}$$

with the flux given by

$$\begin{aligned} J^+ &= -D^+(C^+)\nabla C^+ + D_v^+(C^+)\left(\sum_{i=0}^{n} E_i\right)\nabla\left(\frac{C^+}{\rho_S^+ - C^+}\right) \\ &\quad -D_v^+(C^+)\nabla\left(\sum_{i=1}^{n}\frac{(E_i^{ini})}{De_i}\int_0^{t^+} e^{-\frac{s-t}{De_i}}\frac{C^+(s)}{\rho_S^+ - C^+(s)}ds\right). \end{aligned} \tag{39}$$

In Figure 9 and 10 we used (38) to plot M_{t^+} as a function of E_0 and J^+ as a function of D_{e_1} respectively, with D_v^+ defined as in (32). As in Figure 8 M_t^+ is a decreasing function of the parameters showing an accurate physical behavior. Comparing the plots in Figures 5 and 6 with the plot in Figure 10 we observe a significant sensitivity of the flux as a function of the Deborah number D_{e_1}. The model is more sensible to changes in the parameters because when we consider the $E_i's$ to be constant the non-Fickian part of (38) is more significant.

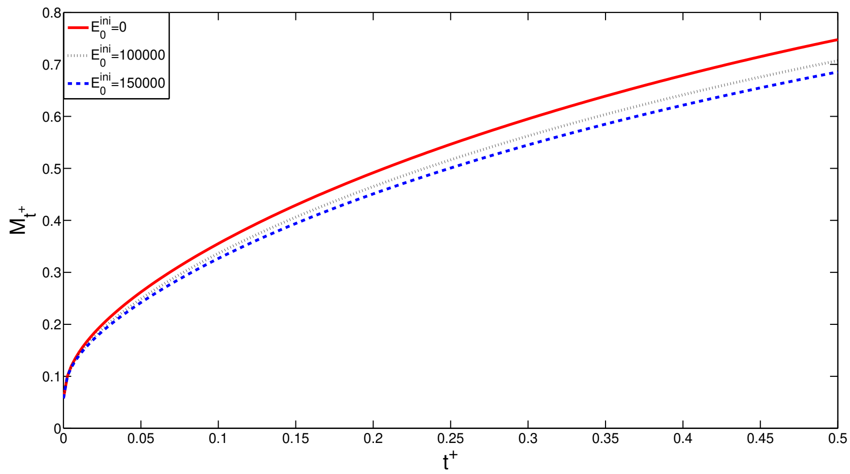

FIGURE 9. M_{t^+} as a function of E_0 for $E_1^{ini} = 2\times 10^5$ Pa and $D_{e_1} = 0.1$

Finally it is worth mentioning that as we can observe in Figures 5 and 10 even for the simple case of one Maxwell element in parallel with a free spring we do not obtain unrealistic oscillations.

4. Conclusions

A non linear non-Fickian model for sorption of a solvent into a polymeric sample is proposed. The main idea is a new interpretation of the non-Fickian

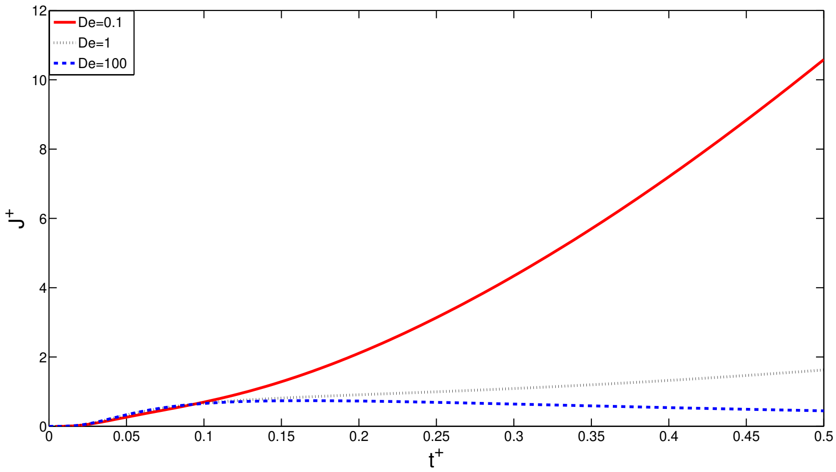

FIGURE 10. J^+ for $x^+ = 0.5$ as a function of D_{e_1} with $E_0^{ini} = 1 \times 10^5\ Pa$ and $E_1^{ini} = 2 \times 10^5$

flux which lead to the establishment of a non linear functional relations for the strain ϵ, the viscoelastic diffusion coefficient D_v and the Young modulus E_i, for $i = 0, 1, ..., n$.

The great advantage of this model consists in the possibility of easily and directly incorporating experimental rheological information about polymer-solvent system (knowledge of E_i and μ_i). Indeed, the Maxwell-Wiechert model (also called generalized Maxwell model by rheologists) can be used for the viscoelastic characterization of the polymer-solvent system. Due to several reasons [15] the rheological characterization employs shear stresses-deformations to deduce the viscoelastic properties. The typical test (frequency sweep test) consists in applying to the sample a small sinusoidal shear stress (falling into the linear viscoelastic range) of constant maximum value and decreasing pulsation ($\omega = 2\pi f$, $f =$ stress frequency). Thus, it is possible measuring the elastic and viscous properties of the sample through the determination of the dependence of the elastic (G') and the viscous (G'') moduli on ω. These experimental trends can be simultaneously fitted by the theoretical G' and G'' trends descending from the solution of the Maxwell-Wiechert model:

$$G' = G_0 + \sum_{i=1}^{m} G_i \frac{(\tau_i\omega)^2}{1+(\tau_i+\omega)^2}, \quad G_i = \eta_i/\tau_i \ ; \tag{40}$$

$$G'' = \sum_{i=1}^{m} G_i \frac{\tau_i\omega}{1+(\tau_i+\omega)^2} \ , \tag{41}$$

where G_i, μ_i and τ_i represent, respectively, the spring constant, the dashpot viscosity and the relaxation time of the i^{th} Maxwell-Wiechert element. As, usually [15], equations (40) and (41) fitting is performed assuming that the relaxation times (τ_i) are scaled by a factor 10. Model fitting parameters are $(m+2)$ (i.e. G_0, the $G_i's$ and μ_1 or τ_1). The exact number m of Maxwell-Wiechert elements is obtained by minimizing the product $\chi^2(2+m)$, where χ^2 is the sum of the squared errors [5].

Assuming to be in the linear viscoelastic range and assuming to deal with an incompressible material (this is typical for polymer based matrices), it is easy to demonstrate that $E_i = 3G_i$ for every i, being the relaxation times, τ_i, the same [15]. Thus, in (6), the parameters connected to the system stress-deformation state can be experimentally determined. Furthermore, the determination of G' and G'' corresponding to different solvent concentrations C, can provide the C dependence of G_0, G_i and τ_1. In other words, all the parameters in the model can be measured or theoretically deduced on the basis of physical considerations. Thus, the model can be used for data fitting but also for predicting the swelling behavior of polymeric matrices.

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