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 as to represent an opposition of the polymer to the Fickian diffusion. Several numerical examples show the effectiveness of the model.

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 diffusion is much smaller than the rate of relaxation the transport is well described by Fick's law. However if the rate of diffusion is of the same order or larger than the relaxation of the material Fick's law does not represent an accurate description of the phenomenon [17, 18, 19]. 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

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

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 in [2, 3, 5, 6, 7, 11, 13, 15] 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]

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

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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 [14, 15] and in [3, 6, 7] concentration dependent.

One of our main concerns in this paper is to properly understand the meaning of the non-Fickian flux J_{NF}. In [14, 15] 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 $\varepsilon = \eta C$, 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 [14], where D and D_v are assumed constant, and Dv is considered negative.

An analogous model has been studied in [8] 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, 5, 6]. However in these works the viscoelastic behavior is not considered responsible for a negative convective flux and consequently 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} which is physically sound. 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 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

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

To define the stress σ we use a Maxwell-Wiechert model [1, 16] 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

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

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 dependant. We note that in (5) the strain ε caused by the penetrant induces a viscoelastic stress response with opposite sign.
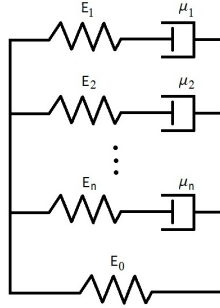

Figure 1: Maxwell-Wiechert model

Replacing (5) in (4) we have

$$\begin{aligned}
\frac{\partial C}{\partial t} &= \nabla \cdot (D(C)\nabla C) \\
&\quad - \nabla \cdot \left(D_v(C)\nabla \cdot \left(\sum_{i=1}^{n} E_i(C) \int_0^t e^{-\frac{1}{\mu_i}\int_s^t E_i(C(r))dr} \frac{\partial \varepsilon}{\partial s}(s)ds \right) + D_v(C)\nabla \cdot (E_0(C)\varepsilon) \right) \ .
\end{aligned} \tag{6}$$

Equation (6) is completed with the initial condition

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

and the boundary conditions

$$\begin{aligned}
C &= C_{in} \text{ on int}(\Gamma^{in}) \times (0,T] \ , \tag{8} \\
J(C) \cdot \eta &= 0 \text{ on int}(\Gamma^{out}) \times (0,T] \ , \tag{9}
\end{aligned}$$

3

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

$$J(C) = -D(C)\nabla C + D_v(C)\nabla \cdot \left(\sum_{i=1}^{n} E_i(C) \int_0^t e^{-\frac{1}{\mu_i}\int_s^t E_i(C(r))dr} \frac{\partial \varepsilon}{\partial s}(s)ds \right) + D_v(C)\nabla \cdot (E_0(C)\varepsilon) . \quad (10)$$

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

A Fujita-type [10] exponential dependence for $D(C)$ is assumed with

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

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 [8, 14, 15] consider D_v constant and negative while in the works [2, 3, 5, 6, 7, 11] 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 v. Then the non-Fickian flux J_{NF} can be interpreted as a convective field of form

$$J_{NF} = vC . \quad (12)$$

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 [20] we have

$$v = -K\nabla p , \quad (13)$$

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

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

where r_f is the fiber radius, α is the concentration dependent porosity, μ is the solvent viscosity and G is the Kozeny constant.

As the convective field is induced by the stress we have

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

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

$$D_v(C) = KC . \quad (15)$$

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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

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

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. 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 the 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 $C = 0$.

2.3 Non linear viscoelasticity

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

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

we have

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

which leads to

$$\varepsilon = \frac{V_S}{V_0} .$$

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

$$\varepsilon = \frac{m_S}{\rho_S V_0} . \tag{21}$$

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 $C = \frac{m_S}{V_0 + V_S}$, then from (21) we easily deduce that $\varepsilon = f(C)$ with

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

From (6) after integrating by parts we obtain

$$\frac{\partial C}{\partial t} = \nabla \cdot \left(D(C)\nabla C - D_v(C)\nabla \cdot (\sum_{i=0}^{n} E_i(C)f(C)) + f(0)\sum_{i=1}^{n} E_i(C)e^{-\frac{1}{\mu_i}\int_0^t E_i(C(r))dr} \right)$$

$$+ \nabla \cdot \left(D_v(C)\nabla \cdot \left(\sum_{i=1}^{n} \frac{E_i(C)}{\mu_i} \int_0^t E_i(C(s))e^{-\frac{1}{\mu_i}\int_s^t E_i(C(r))dr} f(C(s))ds \right) \right) . \tag{23}$$

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

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

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

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

(26)

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

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

(27)

As the Young modulus of a polymer is related to the cross-link density by $E = 3\rho_x RT$ [12] 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

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

(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

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

(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

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

(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

$$
C^+ = \frac{C}{C_{in}}, \quad x^+ = \frac{x}{b}, \quad t^+ = \frac{tD_{eq}}{b^2}, \quad \rho_S^+ = \frac{\rho_S}{C_{in}}, \quad f^+(C^+) = \frac{C^+}{\rho_S^+ - C^+},
$$
$$
D^+(C^+) = exp(-\beta(1 - C^+)) \ .
$$

The diffusion coefficient D_v from (15) and (20) are defined as

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

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

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

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

with the initial condition

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

and the boundary conditions

$$\begin{aligned}
C^+(1, t^+) &= 1 \text{ in } (0, T^+] , \tag{35} \\
J^+(C^+(0, t^+)) &= 0 \text{ in } (0, T^+] , \tag{36}
\end{aligned}$$

where

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

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 $\rho_S = 1000 \ kg/m^3$, $C_0 = 20 \ Kg/m^3$, $C_{in} = 350 \ Kg/m^3$, $r_f = 2 \times 10^{-9} \ m$, $\mu = 8,94 \times 10^{-4} \times Pas$, $G = 1 \times 10^{-3}$ and $D_{eq} = 3,74 \times 10^{-9} \ m^2/s$. 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 2 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 $D_{e_1} = 1$, $E_0^{ini} = 1 \times 10^4 \, Pa$ and $E_1^{ini} = 2 \times 10^4 \, Pa$. When D_v is given by (31) a higher opposition to the diffusion is observed. In Figure 3 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 2 when D_v is given by (31) the model predicts a slower sorption of the solvent into the polymeric sample.
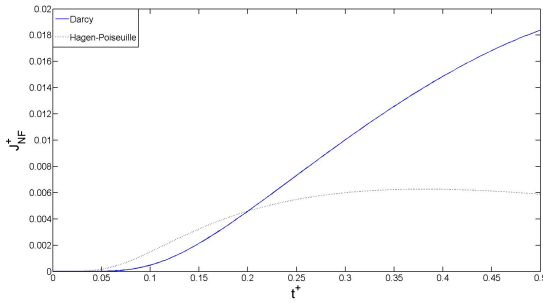
Figure 2: Non-Fickian flux J_{NF} for $x^+ = 0.5$
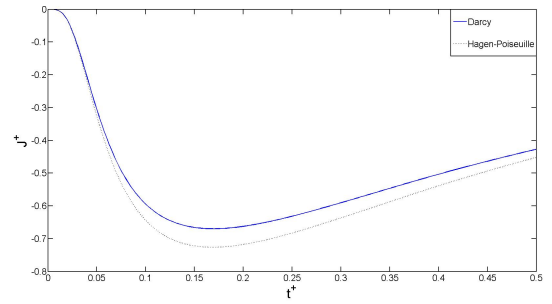
Figure 3: Flux J for $x^+ = 0.5$

In Figures 4 and 5 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 4 we observe an accurate physical behavior since as expected J^+ is an increasing function of D_{e_1}. In Figure 5 we observe that J^+ is not a monotone function of D_{e_1}.
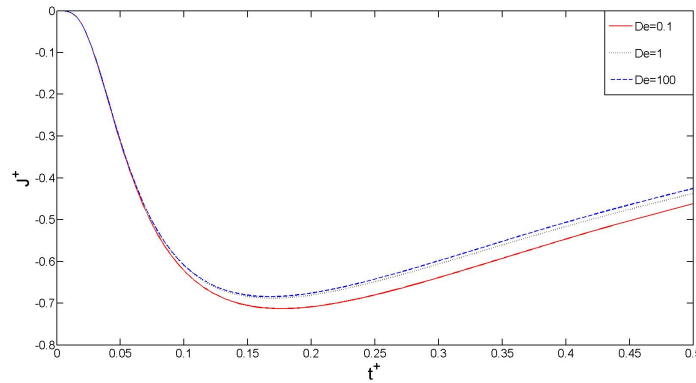

Figure 4: J^+ as a function of D_{e_1} with D_v given by (31), $E_0^{ini} = 1 \times 10^4 \, Pa$ and $E_1^{ini} = 2 \times 10^4 \, Pa$

In Figures 6 and 7 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 function of E_0^{ini}. This is a physically sound behavior since if the material becomes less elastic the solvent will encounter more resistance to diffuse into the polymer.

We note that for the plot of Figure 7 we considered a smaller value of D_{e_1}, since as we can observe on Figure 8 the D_v^+ associated to (32) is smaller than the one that comes from (31). When the weight of the non-Fickian part of the model is too small, the numerical solutions are not sensible to variations in the parameters. Thus a larger Deborah number was considered allowing to observe changes in M_{t^+} as a function of E_0^{ini}.
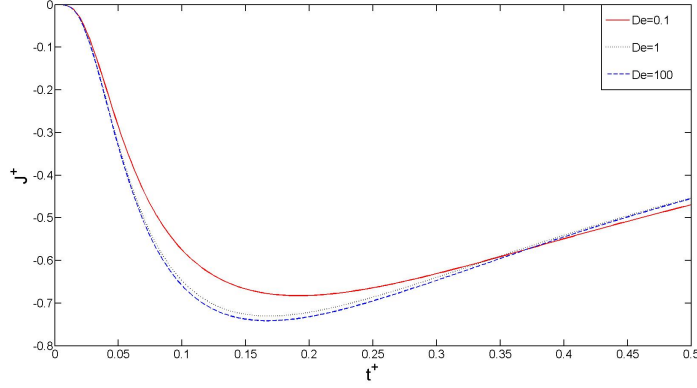
Figure 5: J^+ as a function of D_{e_1} with D_v given by (32), $E_0^{ini} = 1 \times 10^4\ Pa$ and $E_1^{ini} = 2 \times 10^4\ Pa$
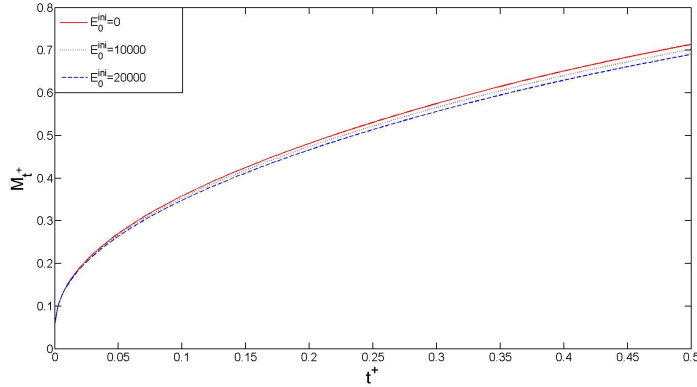

Figure 6: M_{t^+} as a function of E_0^{ini} with D_v given by (31), $E_1^{ini} = 2 \times 10^4\ Pa$ and $D_{e_1} = 1$

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

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

with the flux given by

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

In Figure 9 and 10 we used (38) to plot M_{t^+} as a function of E_0 and D_{e_1} respectively, with D_v^+ defined as in (31). In both plots M_t^+ is a decreasing function of the parameters showing an accurate physical
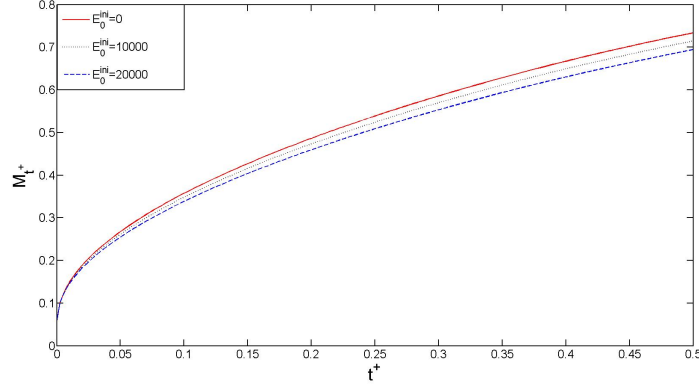
10

Figure 7: M_{t^+} as a function of E_0^{ini} with D_v given by (32), $E_1^{ini} = 2 \times 10^4$ *Pa* and $D_{e_1} = 0.1$
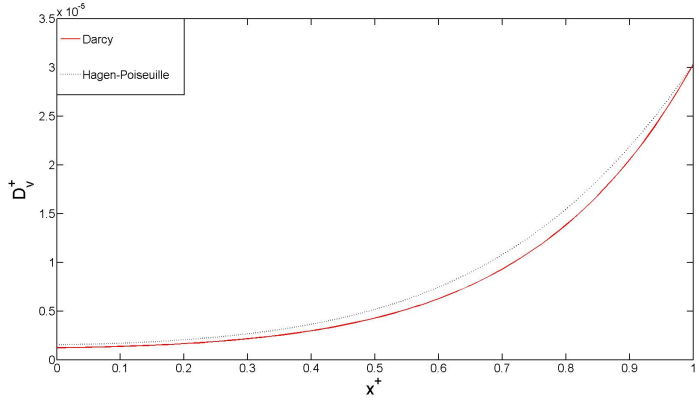

Figure 8: Quantitative comparison of Dv at $t^+ = 0,5$ for $E_0^{ini} = 1 \times 10^4$ *Pa*, $E_1^{ini} = 2 \times 10^4$ *Pa* and $D_{e_1} = 1$

behavior. We note that since the E_i's are non decreasing, the non-Fickian part of (38) is more significant, thus the model is more sensible to changes in the parameters.

Finally it is worth mentioning that as we can observe in Figures 4 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 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 $i = 0, 1, ..., n$. Several numerical examples are presented showing a sound physical behavior. No spurious oscillations are observed even when only one Maxwell fluid arm is coupled in parallel with a free spring [12].
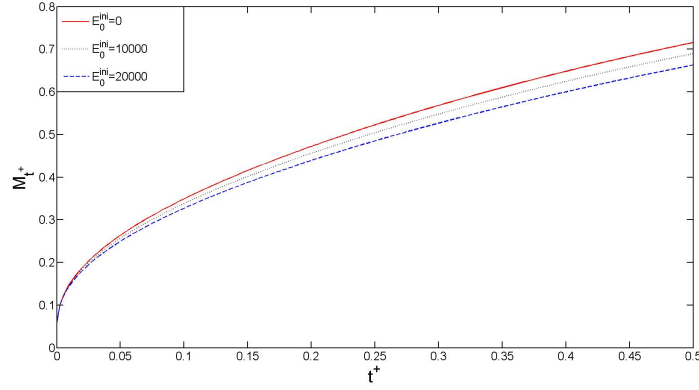
Figure 9: M_{t^+} as a function of E_0 for $E_1^{ini} = 2 \times 10^4$ Pa and $D_{e_1} = 1$
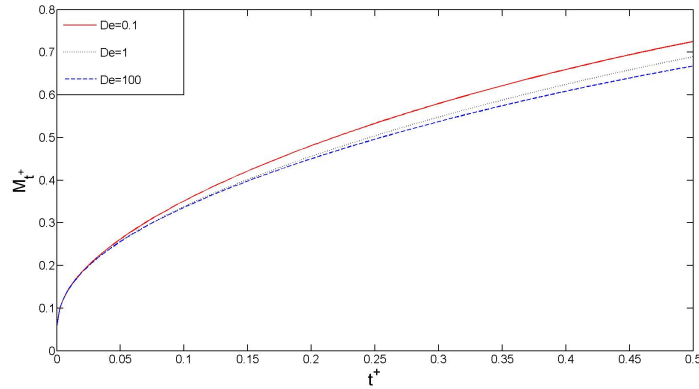

Figure 10: M_{t^+} as a function of D_{e_1} with $E_0^{ini} = 1 \times 10^4$ Pa and $E_1^{ini} = 2 \times 10^4$

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