A MESOSCOPIC MODEL OF MASS TRANSPORT THROUGH IMMISCIBLE BLENDS OF TWO RHEOLOGICALLY DIFFERENT POLYMERS

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Abstract

In this paper, we model, on the mesoscopic level of description, the nonstandard behavior of mass transport into a binary mixture of two immiscible and rheologically different polymers. We formulate a model which explicitly incorporates the coupling between diffusion and the deformation of the interface and also of the two polymers. We use, for this purpose, four microstructural state variables, namely a scalar surface area Q and a covariant anisotropy second-rank tensor **q** for the dividing interface, and two contravariant symmetric second order conformation tensors **A** and **B** for the two immiscible polymers. A new expression for a 1D diffusion mass flux density is derived which involves four coupling functionnals. The results presented here show the possible occurrence of a non-Fickian behavior, in particular when the three involved diffusion Deborah numbers approach the unit.

Keywords: *Non-Fickian diffusion, Viscoelastic swelling, Interface, The polymer conformation***.**

1.   Introduction

Crudely speaking, polymeric blends might be classified into miscible and immiscible ones. However, most of the processed polymers are incompatible to each other and when mixed, they form a blend embedding an inside complex dividing interface whose morphology plays a key role in the mechanical as well physical properties of the final by-product. Obviously, any dynamical processes, in particular those related to mass transport, that affect the interface morphology and the polymer microstructure require a thorough investigation [1]. A variety of today's applications such as membrane separation, barriers, controlled-release of pharmaceuticals, and chemical sensors are good candidates for exploiting the use of such complex materials. Past and recent studies have clearly shown that diffusion of small molecules into such media is expected to behave in a way that cannot be reproduced adequately by the classical Fickian Theory [1,3, 4]. Several experimental observations [2] (and references therein) corroborate such a fact and the deviations from the Fickian kinetics are termed in the literature non-Fickian or viscoelastic diffusion.

Here, in this paper, we aim at generalizing the Fickian theory by incorporating the effects of the internal microstructure on diffusion. First, we extend the Fick first law by adding four new structural state variables and write down the corresponding free energy density. Then we discuss and solve numerically five coupled and non linear 1D time evolution partial differential equations that describe diffusion of a solvent into a blend of two polymers separated by an embedded interface. The model also provides an expression for the internal stresses created by swelling and produced by the internal diffusion mass fluxes. Computations were carried out for two blends: Poly (isobutylene) PIB/Poly (Dimethylsiloxane) PDMS and of Polypropylene PP/ Poly (methyl methacrylate) PMMA. The non-Fickian behavior is expected to occur when the involved different characteristic time scales are of similar magnitudes.

2.   Model

As a starting point, let us specify the appropriate state variables necessary to describe our complex mixture consisting of a solvent and a blend of two immiscible polymers A and B having different rheological properties and embedding and internal complex interface. We will restrict our study to the situation corresponding to the absence of an external flow and assume overall incompressibility under mechanical equilibrium. The state variables are therefore as follows:

- The solvent is characterized by its mass fraction: $c(r,t)$.
- The embedded interface is described by:
    - a scalar surface area density: $Q(r,t)$
    - a traceless covariant anisotropy tensor: $\boldsymbol{q}(r,t)$.
- Polymer A is described by a contravariant conformation tensor : $\boldsymbol{A}(r,t)$
- Polymer B is described by a contravariant conformation tensor : $\boldsymbol{B}(r,t)$

Where **r** is the position vector and t stands for time. All these tensors are second-order and symmetric state

variables. The set of the independent state variables for our system can thus be written as:

$$X = (c, Q, q, A, B) \qquad (1)$$

Now, we specify the internal free energy density for the whole mixture $\{solvent + Blend\ (B/A)\}$ under consideration as:

$$\varphi = \frac{RT}{\Omega_s}\big(c \ln c + \chi c(1 - c)\big) + (1 - c)\Gamma(c)Q$$
$$+ \frac{(1 - c)(1 - \phi)\ G_A(c)}{2}\big(trf(c)\tilde{A} - \ln(\det f(c)\tilde{A})\big) \qquad (2)$$
$$+ \frac{(1 - c)\phi\ G_B(c)}{2}\big(trf(c)\tilde{B} - \ln(\det f(c)\,\tilde{B})\big)$$

The first two terms express the mixing part of the energy between the solvent molecules and the polymeric components, where R is the gas constant; T is the experimental temperature; Ω_s is the solvent molar volume and χ is the Flory-Huggins interaction parameter. The third term is the excess free energy attributed to the interface and Γ is the interfacial tension. The last two terms represent the elasticity of both polymers A and B expressed here by their normalized state variables $\tilde{A}$ and $\widetilde{B}$ to be defined in the next section. In expression (2), we have introduced the functional $f(c) = (1 - c(2 - c_{eq}))$ to express the smooth transition between the two equilibrium states of the whole mixture under consideration and corresponding to $c = 0$ (initial state) and $c = c_{eq}$ (final state). Expression (2) also involves the elasticity moduli $G_A(c)$ and $G_B(c)$ for both polymers and the volume fraction ϕ of polymer B within the blend.

Recall that Fick first law stipulates that the mass flux is a vector proportional to the gradient of concentration. Following the non-equilibrium considerations, the mass flux in complex media is rather related to the gradient of the exchange chemical potential. Thereby, the solvent mass flux density expression is extended and is written as follows:

$$J = -\rho D\left(\frac{\partial c}{\partial x} + \mathbb{A}_1 \frac{\partial Q}{\partial x} + \mathbb{A}_2 \frac{\partial q}{\partial x} + \mathbb{A}_3 \frac{\partial A}{\partial x} + \mathbb{A}_4 \frac{\partial B}{\partial x}\right) \qquad (3)$$

where ρ stands for the constant global mass density and D is the diffusivity coefficient. Expression (3) also involves four functionals, $\mathbb{A}_i, (i = 1,2,3,4)$ that couple diffusion to the microstructure deformation. The mass conservation equation of the solvent in the whole mixture is given by:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\left(\frac{\partial c}{\partial x} + \mathbb{A}_1 \frac{\partial Q}{\partial x} + \mathbb{A}_2 \frac{\partial q}{\partial x} + \mathbb{A}_3 \frac{\partial A}{\partial x} + \mathbb{A}_4 \frac{\partial B}{\partial x}\right)\right) \qquad (4)$$

This equation is expressed in terms of the already defined structural variables and we need to close the set of the governing equations that we express in a one dimensional setting and use the free energy expression (2) to express the physics of our particular system. Therefore:

Interface variable Q:

$$\frac{\partial Q}{\partial t} = \frac{J}{\rho(1 - c)}\frac{\partial Q}{\partial x} + \left(q + \frac{Q}{3}\right)\frac{\partial}{\partial x}\left(\frac{J}{\rho(1 - c)}\right)$$
$$- \frac{(1 - c)}{\tau_{Qq}}\left(\frac{\Gamma(c)}{\Gamma_0}\big(Q - Q_{eq}(c)\big)\right) \qquad (5)$$

Interface variable q:

$$\frac{\partial q}{\partial t} = \frac{J}{\rho(1 - c)}\frac{\partial q}{\partial x} + \left(q - \frac{q^2}{Q} + \frac{4Q}{9}\right)\frac{\partial}{\partial x}\left(\frac{J}{\rho(1 - c)}\right)$$
$$- \frac{(1 - c)}{\tau_{Qq}}\left(\frac{\Gamma(c)}{\Gamma_0}\right)\big(q - q_{eq}(c)\big) \qquad (6)$$

Where, τ_{Qq} is the interface relaxation characteristic time scale and $\Gamma_0 = \Gamma(c = 0)$ refers to interfacial tension at the initial dry blend.

Polymer conformation A:

$$\frac{\partial A}{\partial t} = \frac{J}{\rho(1 - c)}\frac{\partial A}{\partial x} - A\frac{\partial}{\partial x}\left(\frac{J}{\rho(1 - c)}\right)$$
$$- (1 - c)\left(\frac{(1 - \phi)}{\tau_A}\big(f(c)\tilde{A} - 1\big) + \frac{\phi}{\tau_{AB}}\big(f(c)\tilde{B} - 1\big)\right) \qquad (7)$$

Polymer conformation B :

$$\frac{\partial B}{\partial t} = \frac{J}{\rho(1 - c)}\frac{\partial B}{\partial x} - B\frac{\partial}{\partial x}\left(\frac{J}{\rho(1 - c)}\right)$$
$$- (1 - c)\left(\frac{\phi}{\tau_B}\big(f(c)\tilde{B} - 1\big) + \frac{(1-\phi)}{\tau_{AB}}\big(f(c)\tilde{A} - 1\big)\right) \qquad (8)$$

Where τ_A is the relaxation characteristic time scale of the polymer conformation A (respectively, τ_B for polymer conformation B). On the same footing, τ_{AB} designates a time constant that couples between the irreversible processes in the relaxation of both polymers. Of course, in all these equations, (5-8), we need to replace the mass flux J by its expression (3). The model is also supplemented by an expression for the extra stress tensor whose non vanishing components are given by:

$$\sigma_{11} = (1 - c)\Gamma(c)\left(q + \frac{1}{3}Q\right)$$
$$- (1 - c)(1 - \phi)\ G_A(c)\big(f(c)\tilde{A} - 1\big)$$
$$- (1 - c)\phi\ G_B(c)\big(f(c)\tilde{B} - 1\big)$$

$$\sigma_{22} = \sigma_{33} = -\frac{(1 - c)\Gamma(c)}{2}\left(q - \frac{2}{3}Q\right) \qquad (9)$$

3.   Numerical Results

Let us switch to dimensional analysis in order to depict the different time scales involved in this diffusion process and also determine groups of physical parameters that may dictate the behavior of mass transport kinetics. To do so, we introduce the following dimensionless quantities for space and time:

$$\frac{\partial}{\partial x} = \frac{1}{L_0}\frac{\partial}{\partial X} \qquad \theta = \frac{t}{\tau_d} \qquad (10)$$

Where L_0 a characteristic length scale and τ_d is the diffusion characteristic time scale. Similarly, we define dimensionless quantities for the state variables as follows:

$$\tilde{C} = \frac{c}{c_{eq}}$$

$$\tilde{Q} = \frac{Q}{Q_0} \qquad \tilde{q} = \frac{q}{Q_0} \qquad (11)$$

$$\tilde{A} = \frac{A}{A_{eq}} \qquad \tilde{B} = \frac{B}{B_{eq}}$$

Here, c_{eq} is the equilibrium mass fraction; Q_0 the total interfacial area size density at the initial state and A_{eq} and B_{eq} are the equilibrium values for the conformation tensors A and B respectively. The dimensionless forms of the governing equations involve three diffusion-Deborah numbers defined as:

$$De_{Qq} = \frac{\tau_{Qq}}{\tau_d}, \qquad De_A = \frac{\tau_A}{\tau_d} \qquad De_B = \frac{\tau_B}{\tau_d}. \qquad (12)$$

And also four dimensionless groups of physical parameters:

$$g_Q = \frac{\Gamma_0 Q_0 \Omega_s}{RT} \qquad g_q = \frac{\alpha_0 Q_0^2 \Omega_s}{RT}$$

$$\qquad (13)$$

$$g_A = \frac{G_{OA} \Omega_s}{RT} \qquad g_B = \frac{G_{OB} \Omega_s}{RT}$$

As a result, we here present only the calculated normalized mass uptake versus the normalized time for fixed values of the coupling constant ($g_Q = g_q = g_A = g_B = 0,1$) and for two sets of Deborah numbers $(De_{Qq}, De_A, De_B) = (10^{-5}, 10^{-3}, 10^{-3})$ and $(0.009, 0.9 , 0.4)$ (Figure 1). The curves are calculated for two model systems corresponding to the sorption process of methanol MeOH into two different immiscible blends B/A (30/70): PIB/PDMS and PP/ PMMA. We clearly observe an overshoot in the mass uptake when the polymers Deborah numbers are approaching the unit. Even for very small values of the Deborah numbers, diffusion is still non Fickian and does not follow the square root kinetics predicted by the Fickian theory. The profiles of all

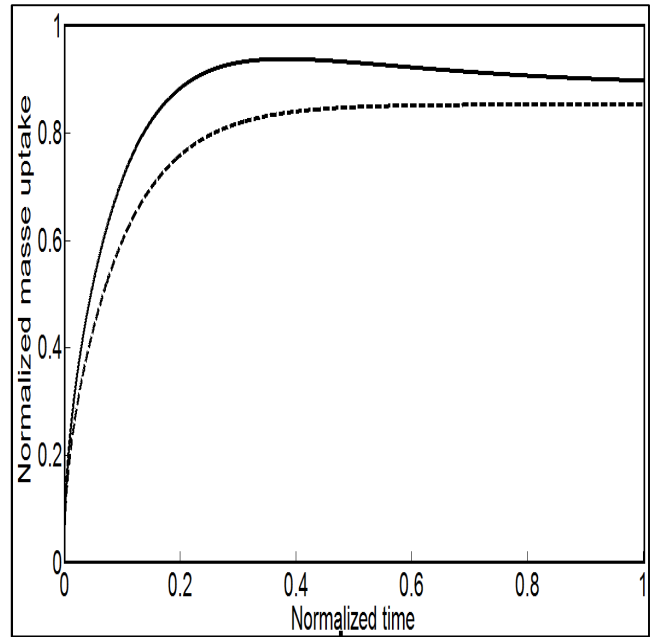the model state variables are calculated both locally and globally.

Figure 1: Polymer mass uptake vs normalized time. Dashed line: $(De_{Qq}, De_A, De_B) = (10^{-5},\ 10^{-3}, 10^{-3})$ and Solid line: $(De_{Qq}, De_A, De_B) = (0.009, 0.9 , 0.4)$.

4.   Conclusion

In the present study, we have discussed, via modeling and numerical resolution, the probable occurrence of the non-Fickian behavior in a complex mixture consisting of a simple fluid and an immiscible blend of two rheologically different polymers. Five new coupled time evolution equations are developed and solved numerically. Scaling analysis shows the presence of three diffusion Deborah numbers and four coupling constants whose influence appears to be very significant. When the Deborah numbers approach the unit, diffusion is no longer Fickian but exhibits, as expected, a non-Fickian character.

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