Dynamics and Thermodynamics of Mass Transport in Polymeric Mixtures with Complex Interfaces

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DYNAMICS AND THERMODYNAMICS OF MASS TRANSPORT IN POLYMERIC MIXTURES WITH COMPLEX INTERFACES

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Abstract: *In this contribution, we model, at the mesoscopic level of description, the non-standard mass transport of a solvent in a mixture of two immiscible polymers. We formulate a model that explicitly integrates the coupling between diffusion and the deformation of the interface and the macromolecular chains as well. For this purpose, in addition to the solvent mass fraction c, we use two symmetrical tensors of order two: the interface tensor* ***N*** *and the conformation tensor* ***m****. We predict profiles of these state variables in addition to those of the stress tensor created by diffusion.*

Mots clés *: mass transport-Interface-conformation-sorption.*

1. Model

1.1 State variables

As a starting point, let's specify the appropriate state variables to describe our mixture which is composed of two viscoelastic polymers separated by an interface (complex medium) and a solvent (simple fluid). The diffusion process studied is that which corresponds exclusively to the interpenetration between the solvent and the immiscible mixture. Any mutual diffusion between the two polymers is ignored and, consequently, the two polymers retain their immiscibility. We will limit our study to the isothermal case and in the absence of an external flow. In this perspective, the state variables that we choose to describe our system are: the mass fraction c of the solvent, the second order tensor of interface **N**, and the second order conformation tensor of polymer **m**.

The tensor **N** and the normalized tensor **m** are written in the case of a unidirectional diffusion as follows:

$$\boldsymbol{N} = \begin{pmatrix} N_1 & 0 & 0 \\ 0 & N_2 & 0 \\ 0 & 0 & N_2 \end{pmatrix}, \boldsymbol{m} = \begin{pmatrix} m & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad (1)$$

1.2 Free energy

The internal free energy has three contributions. The first is attributed to the mixing, the second to the excess energy brought by the presence of the interface, and the third is attributed to the conformation of the polymer blend:

$$\varphi(c, N_1, N_2, m) = \varphi^{mix}(c) + \varphi^{interface}(c, N_1, N_2) + \varphi^{conformation}(c, m) \qquad (2)$$

The first is given by the Flory-Huggins theory:

$$\varphi^{mix}(c) = \frac{RT}{\Omega_s}\left(c \ln c + \frac{(1-c)\ln(1-c)}{x_n} + \chi c(1-c)\right) \qquad (3)$$

Where R is the gas constant, T is the temperature, Ω_s is the molar volume of the solvent and χ is the Flory interaction parameter. The second contribution is due to the interface and is given by [1]:

$$\varphi^{interface}(c, N_1, N_2) = (1-c)\Gamma(c)\mathrm{tr}(N) \qquad (4)$$

Where Γ is the interfacial tension. The third contribution is due to the elasticity of the macromolecular chains.

$$\varphi^{conf}(c, m) = \frac{G_0}{2}(1-c)[f(c)m - \ln(f(c)m))] \qquad (5)$$

where $f(c) = 1 - c(2 - c_{eq})$, G_0 the modulus of elasticity is, K_B is Boltzmann's constant, H_B is the constant of stiffness, m is the conformation of macromolecular chains, and c_{eq} is the equilibrium concentration. Note that the driving force of spontaneous diffusion is the gradient of the chemical potential as required by non-equilibrium thermodynamics, which can be written as:

$$\tilde{\mu}_s - \tilde{\mu}_0 = \varphi + (1-c)\left(\frac{\partial\varphi}{\partial c}\right) - m\left(\frac{\partial\varphi}{\partial m}\right) \qquad (6)$$

1.3 Governing equations

Generalizing Fick's first law, mass flux density is written as :

$$J = -\rho D\left(\frac{\partial c}{\partial x} + \mathbb{E}_1\frac{\partial N_1}{\partial x} + \mathbb{E}_2\frac{\partial N_2}{\partial x} + \mathbb{F}\frac{\partial m}{\partial x}\right) \qquad (7)$$

D is the diffusivity and ρ is the constant mass density of the overall system. In addition, equation (7) shows three coupling constants:

$$\begin{aligned} \mathbb{E}_1(c, N_1, N_2, m) &= (\partial\mu_s/\partial N_1)/\ (\partial\mu_s/\partial c) \\ \mathbb{E}_2(c, N_1, N_2, m) &= (\partial\mu_s/\partial N_2)/\ (\partial\mu_s/\partial c) \\ \mathbb{F}(c, N_1, N_2, m) &= (\partial\mu_s/\partial m)/\ (\partial\mu_s/\partial c) \end{aligned} \qquad (8)$$

that are three functions dependent on the state variables c, N and m and which couple diffusion to dynamic changes of the micro-structure of the system. The solvent continuity equation in the polymer blend reads as follows:

$$\frac{\partial c}{\partial t}=\frac{\partial}{\partial x}\left(D\left(\frac{\partial c}{\partial x}+\mathbb{E}_1\frac{\partial N_1}{\partial x}+\mathbb{E}_2\frac{\partial N_2}{\partial x}+\mathbb{F}\frac{\partial m}{\partial x}\right)\right) \tag{9}$$

Thermodynamically, the Fickian diffusion is described by one single state variable, namely the concentration c of the solvent. Here, the continuity equation depends on three other structural variables. To close the system of equations, we introduce the evolution equations for the structural variables N_1 and N_2 [1] and m as follows:

$$\frac{\partial N_1}{\partial t}=\frac{J}{\rho(1-c)}\frac{\partial N_1}{\partial x}+N_1\frac{[N_1+4N_2]}{N_1+2N_2}\frac{\partial}{\partial x}\left(\frac{J}{\rho(1-c)}\right)-\frac{(1-c)}{\tau_N}\frac{\Gamma}{\Gamma_0}\left(N_1-N_{1eqf}\right) \tag{10}$$

$$\frac{\partial N_2}{\partial t}=\frac{J}{\rho(1-c)}\frac{\partial N_2}{\partial x}-\frac{[N_1N_2]}{N_1+2N_2}\frac{\partial}{\partial x}\left(\frac{J}{\rho(1-c)}\right)-\frac{(1-c)}{\tau_N}\frac{\Gamma}{\Gamma_0}\left(N_2-N_{2eqf}\right) \tag{11}$$

$$\frac{\partial m}{\partial t}=\frac{\partial}{\partial x}\left(\frac{J}{\rho(1-c)}m\right)-m.\frac{\partial}{\partial x}\left(\frac{J}{\rho(1-c)}\right)-\left(\frac{\partial}{\partial x}\left(\frac{J}{\rho(1-c)}\right)\right).\,m-\frac{(1-c)}{\tau_m}\left(\frac{m}{(k_BT/H)}-I\right) \tag{12}$$

The parameters τ_N and τ_m are the relaxation times of the polymer blend, $\Gamma_0=\Gamma(c=0)$ is the initial state value of the dry polymer and N_{ieqf} is the value of N_i in the final equilibrium state.

2. Scaling analysis

We introduce the following dimensionless quantities:

$$\frac{\partial}{\partial x}=\frac{1}{L_0}\frac{\partial}{\partial X} \qquad \theta=\frac{t}{\tau_{deq}} \tag{13}$$

respectively for space and time. The quantities L_0 and τ_{deq} refer to the characteristic length and time of diffusion, respectively. We introduce also the following dimensionless variables:

$$\tilde{N}_i=\frac{N_i}{N_0}\ ,\quad \tilde{c}=\frac{c}{c_{eq}}\ ,\quad \tilde{J}=\frac{J}{\rho c_{eq}L_0/\tau_{deq}} \tag{14}$$

Where $N_0=tr\left(N_{eq}(c=0)\right)$. Two coupling constants emerge naturally in the dimensionless equations:

$$g_0=\frac{\Gamma_0 N_0\Omega_S}{RT} \qquad g_1=\frac{G_0\Omega_S}{2RT} \tag{15}$$

We also see appearing, in the dissipative part, the interface diffusion Deborah number D_e, the boundary diffusion Deborah number D_{eb} and the conformation diffusion Deborah number D_{em} :

$$\begin{aligned} D_e &= \frac{1}{K_{bs}\tau_{deq}} \\ D_{eb} &= \frac{\tau_{Nb,0}}{\tau_{deq}} \\ D_{em} &= \frac{\tau_{m,0}}{\tau_{deq}} \end{aligned} \tag{16}$$

3. Numerical results

The numerical resolution of the discretized equations using the the finite difference method, allowed us to calculate the profiles of the concentration, weight gain, swelling and internal stresses created by the local deformation of the interface. We here present only the influence of the Deborah number at the boundaries (Deb) on the swelling (Figure 1).

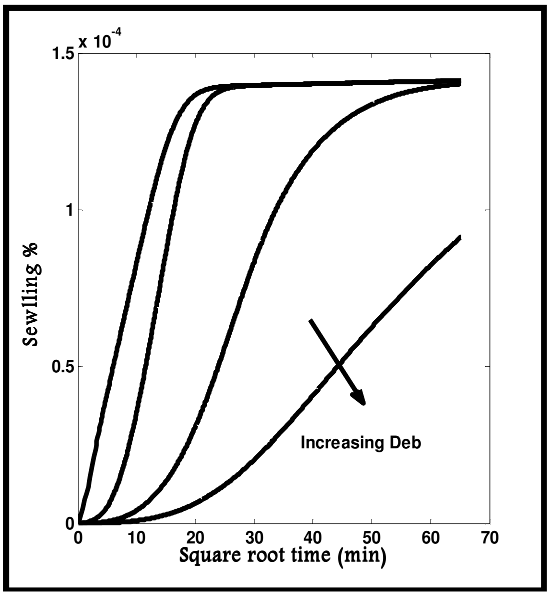

Figure 1 *:Swelling for different values of Deb* (0.001, 0.1, 1 and 2).

Figure 1 shows the macroscopic swelling of the mixture as a function of the normalized time for different values of De (0.001,0.1,1 and 2). We observe that the behavior of mass transport as well as that of dynamic changes in the microstructure (interface + conformation) is strongly influenced by the variation of Deb. For large values of Deb (=1 and 2) the boundary exhibits a viscoelastic behavior, the boundary slows down the passage of solvent molecules through the film and diffusion becomes a process controlled by the boundary adsorption. For small values of Deb (=0.001) the boundary exhibits a Fickean behavior, since the boundary facilitates the passage of solvent molecules through the film surface. Therefore the gradients of the structural variables become negligible compared to the concentration gradient which become the driving force of diffusion.

4. Conclusion

We have generalized Fick's theory to study the mass transport behavior of a solvent in a mixture of viscoelastic immiscible polymers composing a matrix and a dispersed minor phase. The model consists of a set of coupled non-linear equations describing the evolution of the solvent mass fraction c and two structural variables representing dynamic changes in the morphology of the microstructure (interface + conformation). The case of a unidirectional sorption was investigated. The dimensional analysis reveals groups of physical parameters that emerge naturally in the dimensionless equations: two constants characterizing the coupling between diffusion and structure deformation and three diffusion Deborah numbers characterizing the viscoelastic nature of mass transport in the polymeric mixture. Numerical results show that diffusion becomes non-Fickian for large Deb values.

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