# Modeling Non-Fickian Sorption of a Solvent in Immiscible Polymers

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January 22, 2020

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# MODELING NON-FICKIAN SORPTION OF A SOLVENT IN IMMISCIBLE POLYMERS

***Abstract** : We formulate a mesoscopic model to investigate the behavior of a solvent mass transport into an immiscible polymeric blend embedding a complex deformable interface. Under unsteady isothermal conditions, we discuss the diffusion-induced mechanical changes occurring in the blend internal micro-structure and its effect on mass transport which may consequently exhibit a non-Fickian character. Nice agreement was found between the theoretical predictions and experimental data (taken from literature) for the sorption of toluene through polypropylene (PP)/ Acrylonitrile-co-butadiene Rubber (NBR).*

***Key words** : Non-Fickian diffusion, interface-conformation, sorption, swelling*

## 1. Introduction

The study of a solvent mass transport into immiscible polymeric systems is a growing research area [1-3] due to the interesting mechanical as well as physical properties such as barrier, electronic devices, protective coatings, membrane separation processes, drug delivery systems and packaging of foods etc. Our aim in the present study is to derive a mesoscopic 3-D model capable [1] of: i) describing the nonstandard unsteady mass transport of a solvent into an immiscible polymeric blend and ii) providing information regarding the time dependent and equilibrium states of the macromolecular conformation as well as of the size and shape anisotropy densities of the embedded interface. On the mesoscopic level, the thermodynamically compatible derived evolution equations are parameterized by the free energy density and kinetic coefficients. In addition to the mass fraction of the solvent **c**, three additional independent structural state variables are adopted, namely the macromolecular chain conformation tensor **m**; and a scalar **Q** and a second-rank tensor **q** respectively for the size and shape anisotropy of the interface area. The reduction of the 3D-model to the unidirectional case is thoroughly investigated firstly by properly normalizing the governing equations, secondly by solving them numerically and finally by confronting their predictions to experimental data available in literature [3].

## 2. Model formulation

The system under consideration consists of two interpenetrating media, one is a solvent (a simple fluid) and the other is a blend of two immiscible and viscoelastic polymers embedding an internal interface (a complex fluid). The macromolecular chains and the interface deform under diffusion and such a deformation couples to diffusion. Thereby, by requiring the compatibility of thermodynamics, the diffusion mass flux is no longer expressed as proportional to the gradient of concentration but rather to the chemical potential $\mu = \mu(c, Q, q, m)$. In the absence of chemical reactions and flow, the solvent continuity equation can be written under the following form:

$$\rho \frac{\partial c}{\partial t} = -\,\nabla . J \qquad (1)$$

Where $\boldsymbol{\rho}$ is the global mass density, $\boldsymbol{t}$ is the time and the vector J refers to the unsteady diffusion mass flux expressed as:

$$J = -\rho \boldsymbol{D}(\nabla \mathrm{c} + \mathbb{E}\,\nabla\,\mathrm{Q} + \mathbb{H}\colon \nabla \mathrm{q}^{\mathrm{T}} + \mathbb{R}\colon \nabla \mathrm{m}^{\mathrm{T}}) \qquad (2)$$

Which involves four functionals:

$$\boldsymbol{D}(c, Q, q, m) = \frac{c}{\rho \Lambda_J}\left(\frac{\partial \mu_s}{\partial c}\right) \qquad (3)$$

$$\mathbb{E}(c, Q, q, m) = \left(\frac{\partial \mu_s}{\partial Q}\right) / \left(\frac{\partial \mu_s}{\partial c}\right) \qquad (4)$$

$$\mathbb{H}(c, Q, q, m) = \left(\frac{\partial \mu_s}{\partial \mathrm{q}}\right) / \left(\frac{\partial \mu_s}{\partial \mathrm{c}}\right) \qquad (5)$$

$$\mathbb{R}(c, Q, q, m) = \left(\frac{\partial \mu_s}{\partial \boldsymbol{m}}\right) / \left(\frac{\partial \mu_s}{\partial c}\right) \qquad (6)$$

Where $\Lambda_J$ refers to the inverse of the J-relaxation time, $\mu_s$ is the solvent chemical potential, $\boldsymbol{D}$ is the diffusivity coefficient, $\mathbb{E}$ is a scalar that couples the effects of mixing to the changes occurring at the size of the interface, the two quantities $\mathbb{H}$ and $\mathbb{R}$ are second-order tensor functions that couple, respectively, the shape anisotropy changes and effects of conformational elasticity to mass transport. A combination of equations (1) and (2) gives the following extended continuity equation for the solvent in the mixture:

$$\rho \frac{\partial c}{\partial t} = \nabla \cdot \big(\rho D(\nabla c + \mathbb{E}\,\nabla Q + \mathbb{H}\colon \nabla q^T + \mathbb{R}\colon \nabla m^T)\big) \qquad (7)$$

To close the set of the governing equation, the governing equation for the size density is as:

$$\frac{\partial \boldsymbol{Q}}{\partial t} = \frac{J}{\rho(1-c)} \cdot \nabla Q + q\colon \nabla \left( \frac{J}{\rho(1-c)}\right)^T + \frac{Q}{3} \nabla \cdot \qquad (8)$$

$$\left( \frac{J}{\rho(1-c)}\right) - \frac{(1-c)^2}{\tau_{qQ}} \Bigg( \big(Q - Q_{eq}\big) +$$

$$\left(\frac{\alpha_0}{\Gamma_0}\right)\left(q-q_{eq}\right):\left(q-q_{eq}\right)\Big)$$

Where $\tau_{qQ}$ is the interface relaxation time, $\alpha_0$ is the shape anisotropy elasticity modulus, $\Gamma_0$ is the interfacial tension and $(Q_{eq}, q_{eq})$ is the final equilibrium for size and anisotropy density respectively. The governing equation for the anisotropy density of the shape of the interface is as:

$$\frac{\partial \boldsymbol{q}}{\partial t}=\frac{J}{\rho(1-c)}\cdot\nabla q+\nabla\left(\frac{J}{\rho(1-c)}\right)^{T}.q+q\cdot \tag{9}$$

$$\nabla\left(\frac{J}{\rho(1-c)}\right)-\frac{qq}{Q}:\nabla\left(\frac{J}{\rho(1-c)}\right)-\frac{2}{3}Iq:$$

$$\nabla\left(\frac{J}{\rho(1-c)}\right)-\frac{1}{3}\left(q+\frac{2Q}{3}I\right)\nabla\cdot\left(\frac{J}{\rho(1-c)}\right)$$

$$+\frac{Q}{3}\left(\nabla\left(\frac{J}{\rho(1-c)}\right)+\nabla\left(\frac{J}{\rho(1-c)}\right)^{T}\right)-$$

$$\frac{(1-c)^2}{\tau_{qQ}}\left(I+\left(\frac{\alpha_0}{\Gamma_0}\right)\left(\frac{qq}{Q}-\frac{{q_{eq}}^2}{Q_{eq}}\right)\right):\left(q-q_{eq}\right)$$

Finally, the time evolution for the conformation tensor is:

$$\frac{\partial m}{\partial t}+\frac{(1-c)}{\tau_m}\left(\frac{\left(1-c\left(2-c_{eq}\right)\right)m}{(k_B T/H_B)}-I\right)= \tag{10}$$

$$\nabla.\left(\frac{J}{\rho(1-c)}m\right)-\left(\nabla\left(\frac{J}{\rho(1-c)}\right)\right)^{T}.m-$$

$$m.\nabla\left(\frac{J}{\rho(1-c)}\right)-m.\nabla\left(\frac{J}{\rho(1-c)}\right)$$

Where $\tau_m$ is the conformation relaxation characteristic time, $k_B$ is the Boltzmann constant, $T$ is the absolute constant temperature and $H_B$ is a characteristic elastic constant. On the other hand, we assume that the elasticity modulus of the shape anisotropy is negligible compared to the interfacial tension ($\alpha_0 \approx 0$). The reduction to simpler models requires us to use dimensionless analysis. Therefore, we choose the direction of diffusion to be along the Eulerian x-coordinate and we introduce the following dimensionless quantities for the state variables, the material coordinate X and time t:

$$\partial_x=\left(\frac{1}{L_0}\right)\partial_X, \theta=\frac{t}{\tau_d}\quad,\ \tilde{J}=\left(\frac{J}{(\rho c_{eq}L_0/\tau_d)}\right), \tilde{c}= \tag{11}$$

$$c/c_{eq}\,, \tilde{Q}=Q/Q_0, \tilde{q}=q/Q_0, \widetilde{m}=m/m_{eq}$$

Where $\mathrm{L}_0$ is a characteristic length scale, $\tau_d$ is the terminal characteristic diffusion time scale, $\mathrm{c_{eq}}$ is the equilibrium value for the mass fraction, $\mathrm{Q}_0$ is the initial size density at the initial state, $\mathrm{m_{eq}}$ is the polymer conformation at the equilibrium state. The dimensionless forms of the governing equations involve:

- the interface Deborah number defined as the ratio of the relaxation characteristic time scale of the polymer to the diffusion characteristic time scale:

$$De_{Qq}=\frac{\tau_{Qq}}{\tau_d} \tag{12}$$

- the conformation Deborah number defined as the conformation relaxation characteristic time scale of the polymer to the diffusion characteristic time scale:

$$De_m=\frac{\tau_m}{\tau_d} \tag{13}$$

and two coupling constant $(\mathrm{g_Q}, \mathrm{g_m})$:

$$g_Q=\frac{\Gamma_0 Q_0\,\Omega_s}{RT} \tag{14}$$

$$g_m=\frac{G_b\,\Omega_s}{2RT} \tag{15}$$

Where $\Omega_s$ is the solvent molar volume, $R$ is the gas constant, $G_b$ is the blend elasticity modulus.

## 3. Results and discussion

In the following, we have solved numerically the coupled equations for the sorption process of a solvent into a thin film, of an immiscible blend composed of droplets dispersed in a continuous polymeric matrix, both possessing identical rheological properties. We can calculate the normalized mass uptake:

$$M(\theta)=\frac{M(t)}{M_\infty}=\int_0^1 c(X,\theta)\left(\frac{F}{F_{eq}}\right)dX \tag{16}$$

Where $F=(1-c)^{-1}$ being the xx-component of the deformation gradient tensor. We discretize and solve the normalized governing equations by using the finite difference method which allows us to obtain and compare the predicted profiles of mass uptake with available experimental data selected from literature [3]. Figure (1) shows the experimental data performed at T=30 °C of the sorption process of toluene in a thermoplastic elastomeric vulcanized isotactic (PP/NBR) at different blend ratios, with which we are comparing our model predictions. The 100 g phase-separated film sample is a 2mm thick sheet with a number-averaged drop radius of the dispersed phase at the dry state $\overline{\mathrm{R}}_0 = 4.08\,10^{-6}\mathrm{m}$ for PP/NBR (70/30) and a corresponding interface size density $\mathrm{Q}_0 = 3\phi_\mathrm{d}/\overline{\mathrm{R}}_0 = (6.25\,10^5\ \phi_\mathrm{d})\,\mathrm{m}^{-1}$. The interfacial tension is of the order of $\Gamma_0 = 3.5\,10^{-3}\,\mathrm{m}^{-1}$. Toluene has a molar volume $\Omega_\mathrm{s} = 10.68\,10^{-5}\,\mathrm{m}^3\mathrm{mol}^{-1}$ and a molar weight $M_s = 92.1\ g\ mol^{-1}$. The results indicate that the pure PP has the lowest mass uptake of toluene certainly due to the presence of a high degree of cristalinity. Contrariwise, the pure NBR exhibits, the maximum uptake and its blending with PP decreases the weight gain of the whole immiscible mixture to intermediate levels situated between those of the pure polymers. As the content of PP increases, the profiles tend to slightly deviate from the Fickian prediction with a quite enhanced effect of the surface boundary on the dynamics of diffusion. The mass-uptake equilibrium saturation plateau is attained slowly as the PP content augments, which is attributed to the inherent material polarity responsible for some kind of resistance to the solvent penetration. Hence the latter provides a very nice agreement between theoretical predictions and experimental data rather than the former.

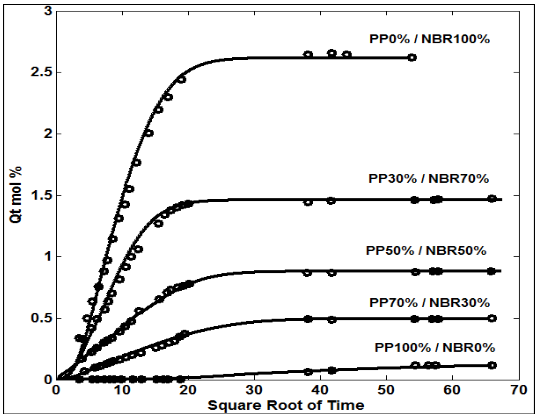

**Figure 1** *: Variation of* $mol\,\%$ *toluene uptake* $(\boldsymbol{Q_t})$ *with square root of time* $(\sqrt{min})$ *of vulcanized PP/NBR immiscible blends. The continuous curves are predicted from our model equations and the curves in (**o**) correspond to the experimental data of the sorption of toluene in a PP/NBR immiscible blend at different compositions at 30℃ [3].*

Figure (2) exhibits the transient net swelling versus the normalized time for different blend ratios.

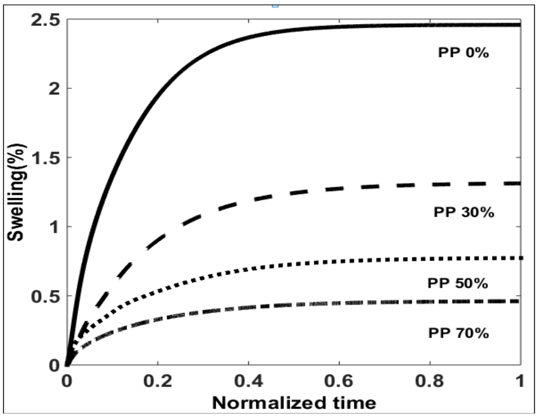

**Figure 2** *: Predicted profiles at different blend ratios against normalized time of transient net swelling.*

The swelling extent of the immiscible blend subjected to diffusion is given by the following expression:

$$L(\theta)-1=\int_0^1 (F-1)\,dX \tag{17}$$

The predicted values for the sorption process of toluene in PP/NBR immiscible blends are 2.459 % for (0/100), 1.317 % for (30/70), 0.776 % for (50/50) and 0.462 % for (70/30). These predicted values, which are remarkably very small, are within the range of expected values since the immiscible mixtures exhibit small values of the solubility at equilibrium. It has been reported in homopolymer films that the behavior of mass transport might be influenced by the correlation between the structure relaxation and the extent of swelling, but no such a study has been performed for immiscible blends.

## 4. Conclusion

In this contribution, we have studied the isothermal mass transport of a simple fluid in a mixture of two immiscible polymers under mechanical equilibrium and in the absence of external flow. The nonlinear formulation extends Fick's laws by the addition of new non-Fickian terms in the diffusion mass flux and also by coupling the time evolution equations of the interface and the macromolecular chain conformation to that of diffusion. The time evolution and constitutive equations are parameterized by the free energy and kinetic coefficients characterizing the system under consideration. Scaling analysis leads to the emergence of several dimensionless groups of physical parameters namely two diffusion Deborah numbers and two coupling constants. Among the predicted results, we show calculated profiles for the swelling at different blend ratios, we also provide calculated profiles for the weight gain. A good agreement is found when comparing the model predictions with sorption data of toluene in a polypropylene (PP)/ Acrylonitrile-co-butadiene Rubber (NBR) blend at different compositions of PP (0%; 30%, 50%, 70%, 100%).

## Acknowledgements:

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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