

# MODELING UNSTEADY PERMEATION THROUGH VISCOELASTIC POLYMERIC MEMBRANES

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## Abstract

As the classical Fickian theory has shown several shortcomings in describing mass transport in complex structured media, we here propose a new model that investigates the permeation behavior of a penetrant through a viscoelastic polymeric membrane. We choose the extra stress tensor as an additional structural state variable to track known the viscoelastic behavior of the polymer. We have modified the nonlinear Maxwell rheological model to incorporate mass transport. A set of two nonlinear coupled and partial differential equations are derived to describe the time evolution of the stress and concentration. Two dimensionless parameters, namely: a diffusion–Deborah number  $De$  and a diffusion–stress coupling constant emerge naturally in the dimensionless form of the governing equations. We have compared our theoretical predictions with experimental data taken from the literature and corresponding to the acetone/rubber mixture. A good agreement is observed.

**Keywords:** *Polymer, Viscoelasticity, Permeation, Stress*

## 1. Introduction

Today, several topical engineering and technological areas exploit the use of the permeation process in their processing. Examples of industrial applications include, but not limited to, packaging, biomedical devices, drug delivery systems etc. Recall that in simple unstructured media such as fluids, solids and rubber polymers, the diffusion process can be well described by the classical Fickian theory expressing that the diffusion mass flux is linearly proportional to the gradient of penetrants concentration. However, in complex media such as glassy polymers and composites, many experimental [1] (and references therein) and theoretical investigations [2-6] have shown that mass transport might markedly deviate from the square root kinetics of the mass-uptake predicted by Fick's laws in a sorption process. This kind of diffusion is called non Fickian or viscoelastic. Indeed, the macromolecular internal structure of the polymer changes locally to accommodate the diffusing small molecules of the solvent and as a result, the polymeric membrane deforms and swells leading to the

creation of internal stresses. This stress-diffusion coupling has since been recognized as the main factor responsible for such observed deviations. In this contribution, we present a viscoelastic model that extends Fick's laws and incorporates explicitly the abovementioned coupling. The governing equations are scaled and two dimensionless numbers are identified: the diffusion-Deborah number and a coupling constant. Finally, we focus on the permeation process of a solvent through a membrane and compare our calculated profiles with experimental data corresponding to the acetone/rubber mixture taken from the literature [6].

## 2. Governing equations

The system considered in this investigation is a two-component mixture composed of a solvent (a simple fluid) and a viscoelastic polymeric membrane (a complex medium). We shall limit ourselves to a one-dimensional flow-free diffusion occurring in binary mixtures kept at a constant temperature and under mechanical equilibrium. To describe our system, we choose the state variables that are the solvent mass fraction  $c$  and the extra stress tensor  $\sigma$ . The solvent mass conservation into the polymer in the absence of chemical reactions is given by the continuity equation.

$$\rho \frac{\partial c}{\partial t} = - \frac{\partial J}{\partial x} \quad (1)$$

where  $\rho$  is the global mass density and  $J$  is the diffusion mass flux density,  $t$  is time and  $x$  stands for the  $x$ -direction of the permeation. By requiring the compatibility of diffusion with non-equilibrium thermodynamics [4-5], the driving force for mass transport is the gradient of the chemical potential;  $\mu = \mu(c, \sigma)$  that is concentration and stress dependent. Thereby, the diffusion mass flux of the solvent particles into the viscoelastic polymer membrane reads as:

$$J = -\rho D(c) \left( \frac{\partial c}{\partial x} - E(c, \sigma) \frac{\partial \sigma}{\partial x} \right) \quad (2)$$

Where  $D(c)$  is the concentration dependent diffusivity coefficient of the solvent and  $E(c, \sigma)$  is a diffusion-stress

coupling functional which also depends on the concentration and on the stress. Note that Equation (2) clearly extends Fick's first law by the addition of a new term which considers the effects of the stress on the transport properties. If the functional  $E$  is equal to zero, equation (2) reduces to the classical Fick's first law. Inserting this non-Fickian mass flux expression (2) into the mass conservation equation (1), we arrive at:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D(c) \left( \frac{\partial c}{\partial x} - E(c, \sigma) \frac{\partial \sigma}{\partial x} \right) \right) \quad (3)$$

To close the set of the governing equations, we introduce, following the point of view of past rheological studies, a non-linear Maxwell-like time evolution equation for the stress that we modify properly to include explicitly diffusion. We then write it down in the following form as:

$$\begin{aligned} \tau_r \left( \frac{\partial \sigma}{\partial t} - \left( \frac{J}{\rho(1-c)} \right) \frac{\partial \sigma}{\partial x} + \sigma \frac{\partial}{\partial x} \left( \frac{J}{\rho(1-c)} \right) \right) + \sigma \\ = \eta_p(c) \frac{\partial}{\partial x} \left( \frac{J}{\rho(1-c)} \right) \end{aligned} \quad (4)$$

Where  $\tau_r$  is the relaxation characteristic time scale of the polymer and  $\eta_p$  is its longitudinal viscosity. Equation (4) characterizes the non-linear viscoelastic behavior of diffusion that is produced by the unsteady swelling of the polymer. The swelling of the polymer membrane as a result of diffusion requires, numerically, an adjustment of the boundary conditions during time when one tries and solves the discretized partial differential equations. To circumvent such a difficulty, we use the Lagrangian (undeformed) coordinate system to be denoted in the following by  $X$  that is related to the Eulerienne (deformed) coordinate  $x$  as follows:

$$dx = F dX \quad (5)$$

where  $F$  is the  $xx$ -component of the second-order deformation gradient tensor in the  $x$ -direction of diffusion. For a unidirectional swelling one easily finds out that:

$$F = \frac{1}{1-c} \quad (6)$$

### 3. Scaling analysis

It is convenient to use the following dimensionless quantities:

$$\tilde{X} = \frac{X}{L_0} \quad \theta = \frac{t}{\tau_d} \quad (7)$$

For space and time respectively, and the following dimensionless quantities for the state variables:

$$\tilde{c} = \frac{c}{c_{eq}} \quad \tilde{\sigma} = \frac{\sigma}{G_0} \quad (8)$$

for the mass fraction and the stress, respectively. The quantity  $c_{eq}$  is the solvent equilibrium mass fraction and  $G_0$  is the matrix elasticity modulus at the initial state (dry polymer). Finally, the dimensionless continuity equation is thus:

$$\frac{\partial \tilde{c}}{\partial \theta} = (1 - c_{eq} \tilde{c}) \frac{\partial}{\partial \tilde{X}} \left( \tilde{D}(1 - c_{eq} \tilde{c}) \left( \frac{\partial \tilde{c}}{\partial \tilde{X}} - E_0 \tilde{E} \frac{\partial \tilde{\sigma}}{\partial \tilde{X}} \right) \right) \quad (9)$$

And the normalized stress time evolution equation reads as:

$$\begin{aligned} \frac{\partial \tilde{\sigma}}{\partial \theta} + \frac{\tilde{\sigma}}{D_e} = -c_{eq}(1 - c_{eq} \tilde{c}) \tilde{D}(c) \left( \frac{\partial \tilde{c}}{\partial \tilde{X}} - E_0 \tilde{E} \frac{\partial \tilde{\sigma}}{\partial \tilde{X}} \right) \frac{\partial \tilde{\sigma}}{\partial \tilde{X}} \\ + c_{eq}(1 - c_{eq} \tilde{c}) (\tilde{\sigma} - \tilde{G}_p) \frac{\partial}{\partial \tilde{X}} \left( \tilde{D} \left( \frac{\partial \tilde{c}}{\partial \tilde{X}} - E_0 \tilde{E} \frac{\partial \tilde{\sigma}}{\partial \tilde{X}} \right) \right) \end{aligned} \quad (10)$$

Equations (9) and (10) involve the following three dimensionless functionals:

$$\begin{aligned} \tilde{D}(c) &= D(c)/D_0 \\ \tilde{E}(c) &= \frac{E(c)}{(V_s/RT)} \\ \tilde{G}_p(c) &= \frac{\eta_p(c)/\eta_{p0}}{\tau_r} \end{aligned} \quad (11)$$

where  $D_0$  is a constant diffusion coefficient,  $\eta_{p0}$  =  $\eta_p(c=0)$  is the polymer viscosity at the dry state,  $V_s$  is the solvent molar volume,  $R$  is the gas constant and  $T$  is the temperature. The dimensionless governing equations involve a coupling constant:

$$E_0 = \frac{V_s G_0}{RT c_{eq}} \quad (12)$$

And a diffusion Deborah number:

$$D_e = \frac{\tau_r}{\tau_d}, \quad (13)$$

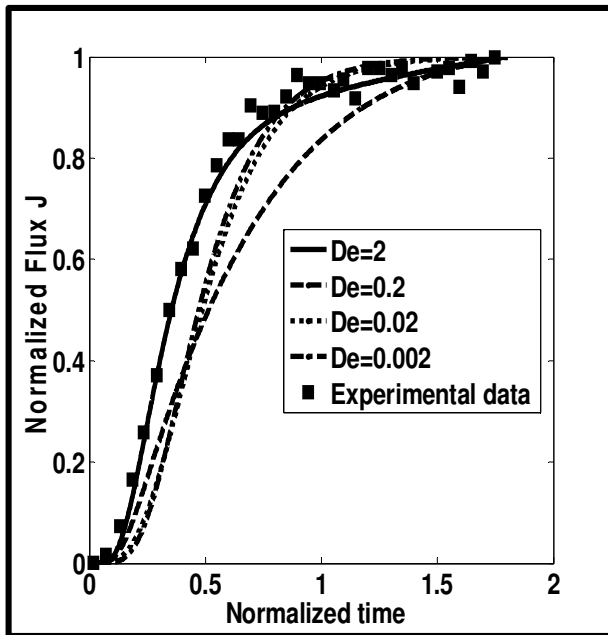
defined as the ratio of the relaxation characteristic time scale of the polymer to the diffusion characteristic time scale  $\tau_d = L_0^2/D_0$ , where  $L_0$  is a characteristic length scale. The non-Fickian or viscoelastic behavior is expected to occur when the diffusion Deborah number is comparable to unit.

## 4. Results and discussion

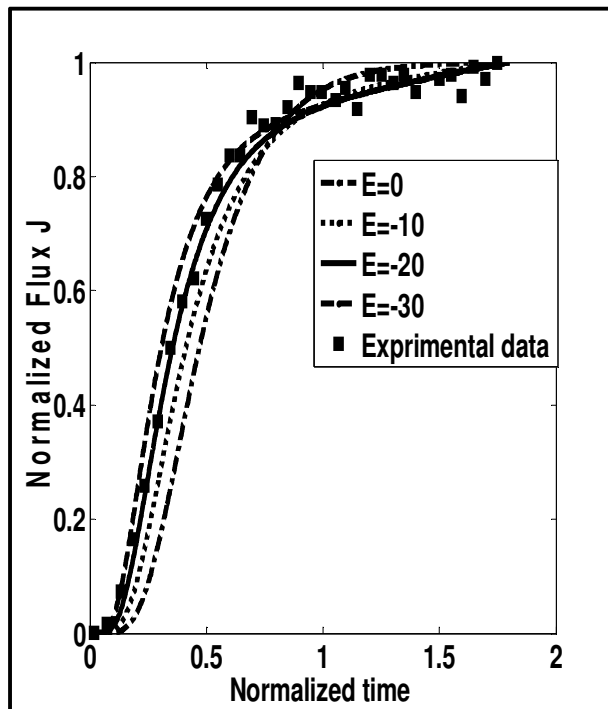
In this section, we present some of the calculated profiles obtained by solving numerically the coupled governing equations using the finite difference method. The profiles correspond to a permeation process of a solvent through a thin film of a viscoelastic polymeric membrane and are compared with the experimental data of acetone-natural rubber system taken from the literature [6].

The normalized non-Fickian diffusion mass flux is shown in Figure 1 for different values of Deborah number  $D_e$ . We observe that the profiles of the unsteady

permeation mass fluxes are influenced by the viscoelastic nature of the membrane. The best fit of the experimental data taken from [6] is obtained for  $D_e = 2$  and  $E_0 = 20$ . Diffusion is clearly viscoelastic.



**Figure 1:** Normalized flux vs normalized time  $\theta$  for different Deborah numbers for  $E_0 = 20$  and  $C_{eq} = 0.09$ . The curve with (■) corresponds to experimental data [6]



**Figure 2:** Normalized flux vs normalized time  $\theta$  for different values of coupling constant and for  $D_e = 2$  and  $C_{eq} = 0.09$ . The curve with (■) corresponds to experimental data [6]

In Figure 2, we vary the coupling constant  $E_0$  and fix the Deborah number to  $De = 2$ . Again the best fit is obtained for  $De = 2$  and  $E_0 = 20$ . The effect of the coupling constant is visible on the permeation flux. The Fickian mass flux ( $E_0 = 0$ ) cannot correctly describe the time evolution of the permeation flux. These results corroborate the fact that mass transport into polymeric membranes is non-Fickian.

## 5. Conclusion

In this contribution, we propose a nonlinear viscoelastic model that describes the kinetics of mass transport of a solvent into a viscoelastic polymeric membrane. We have derived a set of two coupled and non-linear partial differential equations governing the time evolution of two state variables: the solvent mass fraction and the internal stresses created within the polymer. Scaling analysis yields to two dimensionless numbers: a diffusion-Deborah number  $D_e$  and a coupling constant  $E_0$ , whose influence on the permeation process are clearly shown.

We have compared our model predictions with results of experimental observations corresponding to the unsteady permeation process of acetone through a polymeric rubber membrane [6]. A nice agreement is found and diffusion is shown, as expected, to exhibit a non-Fickian character.

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