Solute and Penetrant Diffusion in Swellable Polymers. VII. A Free Volume-Based Model with Mechanical Relaxation

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Synopsis

Penetrant transport through and solute release from continuously swelling polymers is viewed as a process associated with major structural changes in the polymer morphology. Changes in the diffusivities of penetrant and solute reflect a free volume mechanism for transport. The polymer is initially glassy with a uniform dispersion of solute. After the system is placed in contact with a thermodynamically good penetrant, a glassy/rubbery phase transition occurs at a well defined swelling interface. The Fickian equations with concentration-dependent diffusivities and moving boundaries are solved simultaneously in polymer-fixed coordinates. A constitutive relation is used to describe the effect of macromolecular relaxations on the rate of volume expansion as the polymer swells. The penetrant fractional uptake, solute fractional release, sample dimensions, swelling front position, and instantaneous swelling interface number are determined and related to the nature of the swelling process.

INTRODUCTION

A common transport problem in polymer science is the description of the phenomenon of solute diffusion in a medium consisting of a polymer and a penetrant. In this case, a thermodynamically good solvent penetrates a polymer sample and the polymer-penetrant system releases or absorbs a solute. This situation adequately describes the release of an adjuvant from a polymer to a surrounding fluid; this compound is often a plasticizer, an antioxidant, a stabilizer, a residual monomer, an undesirable impurity, or an active agent. The case where the polymer–penetrant medium releases a solute in a controlled manner is of special interest as it has several practical applications. Agricultural uses include the release of pesticides, herbicides, and fertilizers from a polymer base to the surrounding soil. In these cases, the polymer base may degrade into a harmless product during the release of the active agent. Such systems could release germicides and algaecides in a controlled manner into recreational pools as well as preservatives and stabilizers to packaged foods. The leaching of chemical and radioactive waste from polymeric containers buried in storage facilities is also of current concern. An area of particular interest is in pharmaceutical applications where a polymer carrier releases bioactive agents and drugs to visceral fluids.

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Controlled-release polymeric systems could offer a number of potential advantages over the present, conventional means of drug administration. Present methods include single doses or a succession of doses. These are administered either directly to the targeted area, for example by injection, or indirectly, such as by oral administration. Drug delivery is characteristically short in duration, and the amount delivered to the targeted area may deviate from desirable levels of concentration. The potential advantages of polymeric delivery systems include: (i) plasma drug concentration levels maintained in a desirable range; (ii) harmful side effects from systematic administration reduced or eliminated by local administration from a polymer reservoir; (iii) delivery of agents which have short lifetimes in the body facilitated; and (iv) drug delivery extended over long periods of time.

Pharmaceutical controlled-release systems have been classified according to the nature of the triggering cause or the mechanism of drug release.[1,2] These mechanisms include: diffusion, chemical reaction, swelling, osmosis, ultrasound, and magnetic control.

In the swelling controlled-release systems the bioactive agent is dissolved or dispersed within a polymer matrix. The polymer matrix is usually in a dry (or glassy) state so that solute transport through this matrix is very long. If an environmental fluid is a thermodynamically good solvent for the polymer, it penetrates the polymer matrix. The polymer swells and the bioactive agent contained in the swollen region then diffuses through the polymer. Thus, the rate-determining step for the release is the swelling of the polymer.[3,4]

TRANSPORT IN SWELLING POLYMERS

Description of Mechanisms

The system under consideration is a uniform dispersion of solute (subscript 3) in a dry (or glassy) polymer (subscript 2). In the solid state, the rate of solute release from the polymer is negligible. A thermodynamically good solvent (subscript 1) for the polymer is placed in contact with the system. The addition of penetrant leads to considerable volume expansion (swelling) and dramatic amplification of the solute release rate. The dynamic swelling behavior of the polymer, in most cases, controls the mechanism of solute transport through and release from the polymer.[4,5]

The solvent penetration and macromolecular extensions are intimately coupled while the polymer swells from the unperturbed to the solvated state. The increased chain mobility due to chain solvation allows chain extension which results in additional free volume for transport. The penetrant-induced chain extension is a dynamic relaxation phenomenon. The rate at which the polymer chains reorient affects the rate of solvent penetration. Anomalous effects such as two-stage and overshoot sorption[6,7] are possible if the penetrant solubility is dependent on the macromolecular structure. Therefore, penetrant transport and polymer swelling may be strongly amplified by the increase in free volume.

Figure 1 illustrates the solute-penetrant countercurrent transport in a thin slab of initial thickness, $2L_o$. As the polymer undergoes a glassy-rubbery transition at a volume fraction of penetrant, ϕ_g, at the experiment tempera-

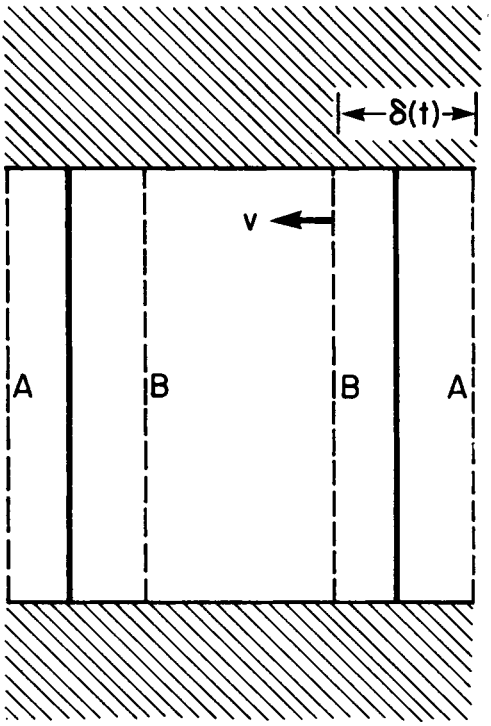


Fig. 1. Schematic representation of the symmetric swelling controlled-release system indicating the polymer interface (A) and the swelling interface (B) for a slab geometry.

ture, a clearly defined front develops between the glassy (unswollen) and rubbery (swollen) regions.[8] This front is known as the swelling interface. An additional front separates the rubbery state from the pure penetrant (polymer interface). The swelling interface moves toward the center line of the sample with a velocity, $v(t)$. The swollen region has a thickness, $\delta(t)$.

From a mathematical point of view, the problem of penetrant transport into the polymer and the associated problem of diffusional solute release from the polymer have been treated using Stefan moving boundary descriptions.[4,9] The Stefan analysis applies the framework of continuum mechanics. Simplified solutions of the penetrant transport with constant volume or with constant diffusion coefficient are available.[10-12] Good,[13] Peppas et al.,[14] Figge and Rudolph,[15] Lee,[16] Frisch,[17] and Korsmeyer et al.[18] have provided general solutions for the solute release problem with various assumptions. All these studies assume the same constitutive relation for both the penetrant and solute fluxes; the product of the component diffusion coefficient and the concentration gradient describes the component flux. None of these treatments predict time-independent solute release or Case II solvent penetration rates.

A complete mathematical analysis of the penetrant transport in swelling systems is not yet available. The main reasons for the lack of rigorous analysis are that (i) modeling problems related to this phenomenon are problems of simple or multicomponent diffusion with moving boundaries: (ii) the diffusion coefficients are coupled and concentration dependent; (iii) the appropriate

constitutive equations for the continuous relaxation of the macromolecular chains during transport must be developed; and (iv) penetrant-induced macromolecular rearrangements affect penetrant transport and solubility. The latter problem is still the subject of the current research efforts of many investigators; some will be described later.

For the penetration of the solvent, a convenient method of analysis is in terms of the diffusional Deborah number, De. It is defined according to Eq. (1), where λ is the characteristic stress–relaxation time of the polymer-penetrant system and θ is the characteristic time for diffusion for the penetrant in the polymer.

$$\mathrm{De} \equiv \frac{\lambda}{\theta} \tag{1}$$

The two characteristic times have their respective definitions given in Eqs. (2) and (3)

$$\lambda \equiv \frac{\int_0^\infty sG(s)\,ds}{\int_0^\infty G(s)\,ds} \tag{2}$$

and

$$\theta \equiv \frac{\delta'^2}{D_{1,s}} \tag{3}$$

where the integrals are over the entire relaxation time spectrum, G is the shear relaxation modulus, δ' is the diffusional path length, and $D_{1,s}$ is the diffusion coefficient of the penetrant in the swollen polymer. Vrentas et al.[19,20] defined regions of Fickian and anomalous transport of the penetrant by calculating the value of De; this value is a function of both temperature and penetrant concentration. For $\mathrm{De} \gg 1$ and $\mathrm{De} \ll 1$ the mechanism is Fickian diffusion. For $\mathrm{De} \gg 1$ the transition to the rubbery state is rate limited and penetration occurs mainly through the glassy, unswollen state. Conversely, for $\mathrm{De} \ll 1$ the penetrant diffusion is rate limited and penetration occurs mainly through the rubbery, swollen polymer. For De of the order of unity, the penetration mechanism is an anomalous transport where macromolecular relaxation during the swelling process is intimately coupled with the solvent penetration.

As in the case of penetrant transport, a complete mathematical analysis of the solute transport in swelling systems is not yet available for similar reasons. Currently, the effect of polymer swelling on solute transport is not well understood. It is useful to extend the mechanism of Fick's law to this situation; that is, the driving force for solute transport is proportional to the gradient of solute chemical potential. Typically, the solute diffusion coefficient is approximately two to three orders of magnitude lower (when expressed in units of cm^2/s) in an equilibrium glassy polymer than in the same polymer swollen in a good solvent. It is reasonable to utilize free volume-dependent penetrant and solute diffusion coefficients throughout the penetrant sorption and solute release.

Peppas and Franson[21] and Hopfenberg et al.[22] proposed that the analysis and prediction of mechanisms of diffusional solute release may be obtained through the swelling interface number, Sw. Its definition is given in Eq. (4)

$$\mathrm{Sw} \equiv \frac{v\delta}{D_{3,s}} \tag{4}$$

where $D_{3,s}$ is the diffusion coefficient of the solute in the swollen phase, and δ is the rubbery phase thickness. This dimensionless number compares the relative mobilities of the penetrant and the solute of macromolecular relaxations in the polymer.

MATHEMATICAL MODELING

A New Model

This section provides a summary of a new model which describes the simultaneous penetrant transport (uptake) and solute release. The constitutive relation for a component flux is given by Fick's law. We consider solute release accompanying large changes in the penetrant and solute diffusivities. The process is modeled as a two-component diffusion in a continuous medium incorporating polymer structural changes in the diffusivity.

The initial thickness, $2L_o$, and penetrant diffusivity in the equilibrium swollen gel, $D_{1,s}$, normalize the position and time scales. The equilibrium and loading concentrations normalize the penetrant and solute concentration variables, respectively.

$$\zeta \equiv \frac{x}{L_o} \tag{5}$$

$$\tau \equiv \frac{D_{1,s}t}{L_o^2} \tag{6}$$

$$\psi_1(\zeta, \tau) \equiv \frac{c_1}{c_{1,s}} \tag{7}$$

$$\psi_3(\zeta, \tau) \equiv 1 - \frac{c_3}{c_{3,d}} \tag{8}$$

Here the subscripts s and d denote equilibrium and initial loading concentrations, respectively. The right-hand side of Eq. (7) holds for constant penetrant molar volumes. Equations (9) and (10) present the transport rate equations for the penetrant and solute, respectively.

$$\frac{\partial \psi_1}{\partial \tau} = \frac{\partial}{\partial \zeta}\left(D_1 \frac{\partial \psi_1}{\partial \zeta}\right) \tag{9}$$

$$\frac{\partial \psi_3}{\partial \tau} = \frac{\partial}{\partial \zeta}\left(D_3 \frac{\partial \psi_3}{\partial \zeta}\right) \tag{10}$$

Initially, the dry polymer has a uniform loading of solute, i.e.

$$\psi_1(\zeta,0) = 0 \tag{11}$$

$$\psi_3(\zeta,0) = 0 \tag{12}$$

and the system is in an infinite sink environment, i.e.

$$\psi_1(-1,\tau) = \psi_1(1,\tau) = 1 \tag{13}$$

$$\psi_3(-1,\tau) = \psi_3(1,\tau) = 1 \tag{14}$$

Although these are typical boundary conditions for the constant volume problem, the reader should note that *the solution uses a polymer-fixed, Lagrangian coordinate system* which allows the system to expand upon swelling. The expansion description ensues later.

The normalized diffusivities are functions simplified from the free volume theory and dependent on penetrant concentration as shown.

$$D_1 = e^{-\beta_1(1-\psi_1)} \tag{15}$$

$$D_3 = \frac{D_{3,s}}{D_{1,s}} e^{-\beta_3(1-\psi_1)} \tag{16}$$

The free volume theory simplification originally proposed by Korsmeyer et al.[18] utilizes coefficients β_1 and β_3 which are material constants. The relative time scales for the penetrant sorption and solute release differ by the ratio of the solute diffusivity in the swollen gel, $D_{3,s}$, to the penetrant diffusivity in the swollen gel, $D_{1,s}$.

The model allows for a differential, Lagrangian volume expansion δQ, according to the amount of penetrant contained in the volume. The two-sided geometry the differential volume element has double-fold symmetry; so that the diffusion problem is one-dimensional in Cartesian coordinates. The principal axis is parallel to the direction of transport and normal to the interface boundaries. The swelling description must include two spatial dimensions

$$\delta Q = \frac{1}{\phi_2} = \delta\alpha_x\delta\alpha_y\delta\alpha_z = \delta\alpha_x\delta\alpha_y\delta\alpha_y \tag{17}$$

In accordance to experimental observations, the dimensionality of swelling, d, changes during penetrant sorption. Despite the large degree of softening associated with the glassy to rubbery phase transition, the presence of a glassy core restricts the rubbery phase to one-dimensional swelling, $d = 1$. At some time, the symmetric swelling interfaces meet at the center of the slab and the glassy core vanishes. This fact removes the one-dimensional swelling constraint due to the drastic decrease of modulus and the swelling continues in an isotropic mode, $d = 3$.

At equilibrium swelling, there exists an amount of penetrant at a volume fraction $\phi_{g,eq}$ which has sufficiently extended and separated the macromolecu-

lar chains to permit mobility and bring about a transition between the polymer glassy and rubbery states. The value of $\phi_{g,eq}$ is determined from thermodynamic interactions between the polymer and penetrant at mechanical equilibrium. Macromolecular mobility is not present in the glassy phase. Since macromolecular extensions occur via relaxational, cooperative motions it does not seem reasonable that the glassy to rubbery phase transition occurs where the local penetrant volume fraction is $\phi_{g,eq}$ at mechanical nonequilibrium. Instead, this model defines the swelling interface at the position, ζ_g, where the local elongation, $\delta\alpha_x$, is equal to the critical elongation, $\delta\alpha_g$. This critical one-dimensional elongation is related to the equilibrium swelling penetrant volume fraction as defined below.

$$\delta\alpha_g = \frac{1}{1 - \phi_{g,eq}} \tag{18}$$

Therefore the swelling interface is defined at the position where the local elongation is equal to the elongation at mechanical equilibrium swelling where the penetrant volume fraction is $\phi_{g,eq}$. Similarly, the instantaneous equilibrium local elongation, $\delta\alpha_{eq,\tau}$, is defined by equation (19).

$$\delta\alpha_{eq,\tau} = \frac{1}{(1 - \phi_1)^{1/d}} \tag{19}$$

It is assumed that the solute volume is negligible. This would be a reasonable assumption at low loadings or small solute specific volumes. Thus, according to Eq. (18) the sum of the penetrant and solute volume fractions is approximately unity.

This formulation accounts for a slow relaxation process which may not be rapid with respect to the overall sorption process. Thus the incremental expansion within a differential volume element is not directly related to the instantaneous penetrant concentration in the simple manner presented in Eq. (19). In order to characterize the time-dependent macromolecular relaxations and expansion, the model uses an assumed constitutive relation for relaxation-controlled volume expansion. The constitutive relation expresses the rate of polymer specific volume change as proportional to the difference between the equilibrium and instantaneous differential specific volumes, $V_{eq,t}$ and V_t, respectively, for any instantaneous local penetrant concentration.

$$\frac{dV_t}{dt} = \frac{V_{eq,t} - V_t}{\lambda} \tag{20}$$

Here the constant of proportionality, λ, is a characteristic relaxation time. The volumes in the constitutive equation are normalized by the initial volume, the times are according to equation (6), and the equation is combined with the relations between volume swelling and local elongation to obtain the final form in Eq. (21).

$$\frac{d(\delta\alpha_\tau)^d}{d\tau} = \frac{(\delta\alpha_{eq,\tau})^d - (\delta\alpha_\tau)^d}{\mathrm{De}} \tag{21}$$

Here the Deborah number, De is defined as

$$\mathrm{De} \equiv \frac{\lambda D_{1,s}}{L_o^2} \tag{22}$$

The Deborah number of Eq. (22) has the same functional form as the Deborah number defined in Eq. (1) and $\delta\alpha_{eq,\tau}$ is the instantaneous equilibrium elongation defined in Eq. (19). The solution of Eq. (21) can be approximated analytically and employed during the numerical implementation of the model.

$$\delta\alpha_{\tau+\Delta\tau} = \left\{ \left(\delta\alpha_{\tau,eq}\right)^d + \left[\left(\delta\alpha_{\tau}\right)^d - \left(\delta\alpha_{\tau,eq}\right)^d\right] \exp\left[\frac{-\Delta\tau}{\mathrm{De}}\right] \right\}^{1/d} \tag{23}$$

This objective, time-discretized, constitutive equation is applied at each polymer-fixed position during an explicit time step integration.

The algorithm provides calculations for further analysis. Since the front velocity and rubbery phase thickness, δ_τ, are generally time dependent, we define an instantaneous swelling interface number, Sw_τ.

$$\mathrm{Sw}_\tau = \frac{v_\tau \delta_\tau}{\bar{D}_3} \tag{24}$$

The instantaneous position, ζ_g, at which $\delta\alpha = \delta\alpha_{g,eq}$ defines the position of the swelling interface. The front velocity, v_τ, is then $d\zeta_g/d\tau$. Crank[23] gives an expression for an average solute diffusivity in the rubbery region as follows:

$$\bar{D}_3 = \frac{\int_{\psi_{1,g}}^{1} D_3(\psi_1)\, d\psi_1}{1 - \psi_{1,g}} \tag{25}$$

The nondimensional concentration of penetrant at the swelling interface, $\psi_{1,g}$, is defined as the local value of ψ_1 where $\zeta = \zeta_g$. Given the penetrant concentration dependence of the solute diffusivity in Eq. (16), the average solute diffusivity in the rubbery region can be calculated analytically using Eq. (26).

$$\bar{D}_3 = \frac{D_{3,s}}{D_{1,s}} \frac{\left[1 - \exp\left(-\beta_3(1 - \psi_{1,g})\right)\right]}{\beta_3(1 - \psi_{1,g})} \tag{26}$$

Thus, it is possible to compute the instantaneous swelling interface number during the model implementation.

NUMERICAL IMPLEMENTATION OF THE MODEL

The dimensionless concentrations ψ_1 and ψ_3 have been defined in the previous section to minimize numerical round-off errors during an explicit time integration. These errors are the result of the addition of small numbers ($\leq 10^{-10}$) to values on the order of unity. This has been observed to be an especially important consideration for small time increments at small times

and for large values of β_1 and β_3. This effect is not important using these dimensionless concentrations until the attainment of 90–95% of final values for both penetrant and solute.

The model was solved using the well-known *method of lines* algorithm for finite differences. The spatial derivatives were approximated by a second-order Lagrangian finite-difference operator allowing the distances between polymer particles to change continuously during the numerical implementation. Time integration was accomplished by a fourth-order Runge-Kutta method.

Convergence was studied for a case consisting of rather stiff model parameters: $\phi_{1,eq} = 0.5$, $\mathrm{De} = 10^{-6}$, $\beta_1 = \beta_3 = 7.0$, $D_{3,s}/D_{1,s} = 10.0$. These values result in large changes in both spatial elongation and diffusivities. The criterion used for convergence is that changes in a plot of M_τ/M_∞ versus τ for both the penetrant and solute are smaller than 0.1% for $M_\tau/M_\infty < 0.80$. The use of 75 spatial nodes and $\Delta\tau = 10^{-5}$ satisfies this criterion for these parameter values. Therefore, these spatial and temporal increments were used in all subsequent calculations for parameter values which seemed to be less stiff.

The accuracy of the method was checked against the analytical solution for the penetrant uptake for constant volume and diffusivity. The required model parameters are $\phi_{1,eq} = 0.0$ and $\beta_1 = 0.0$. The analytical solution is given in equation (27).

$$\frac{M_\tau}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left(-(2n+1)^2\pi^2\tau/4\right) \tag{27}$$

The aforementioned convergence criterion was satisfied easily using only 50 spatial increments and $\Delta\tau = 10^{-5}$.

The interested reader should consult one of the authors for the vector FORTRAN listing of program IBP. This program implemented the model on the Cyber 205 at the Purdue University Computing Center.

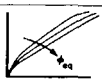
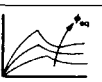
RESULTS AND DISCUSSION

The specification of seven independent parameters results in unique, simultaneous solutions for the penetrant transport and solute release diffusion equations. The parameters are as follows:

1. The material constant which describes the penetrant diffusivity as a function of penetrant concentration, β_1
2. The material constant which describes the solute diffusivity as a function of penetrant concentration, β_3
3. The penetrant volume fraction at which the polymer rubbery/glassy phase transition occurs, ϕ_g
4. The penetrant volume fraction in the equilibrium swollen polymer, ϕ_{eq}
5. The ratio of the solute and penetrant diffusivities in the fully swollen polymer, $\hat{D} \equiv D_{3,s}/D_{1,s}$
6. The ratio of the characteristic relaxation and diffusion times, De

The remainder of this section contains a description of the importance of each

TABLE I

Model Parameter	Solute Fractional Release	Penetrant Fractional Uptake	System Thickness	Front Velocity	Swelling Interface Number, Sw
β_1				An Increase in β_1 Reduces The Front Velocity	An Increase in β_1 Reduces Sw
β_3		No Effect	No Effect	No Effect	An Increase in β_3 Reduces Sw
ϕ_g				No Effect	An Increase in ϕ_g Reduces Sw
ϕ_{eq}				An Increase in ϕ_{eq} Increases The Front Velocity	An Increase in ϕ_{eq} Reduces Sw
$\hat{D}$		No Effect	No Effect	No Effect	An Increase in $\hat{D}$ Reduces Sw
De	An Increase in De Increases Release Rate	An Increase in De Increases Sorption Rate		An Increase in De Reduces The Front Velocity	An Increase in De Reduces Sw

parameter in the model as illustrated by a series of sample solutions. Each set of model solutions contains typical values, such as the time-dependent fractional solute release and penetrant uptake, swelling interface number, system thickness, front velocity, and the order of solute release. Table I contains a summary of the trends observed from several solutions of this model.

The model is sensitive to changes in β_1. When β_1 is zero, the penetrant diffusivity is constant and ordinary, Fickian diffusion is described by the model. Figures 2 through 5 show penetrant and solute concentration profiles for $\beta_1 = 0$ and $\beta_1 = 6.91$. Typically, sharper profiles are attained with high values of β_1. Equation (15) indicates that an increase in β_1 lowers the penetrant diffusivity for any given penetrant concentration. Figure 6 illustrates the penetrant diffusivity concentration dependence at several values of β_1. The penetrant diffusivity is a smooth, increasing function of penetrant concentration, independent of the glassy/rubbery phase regions. At values of $\beta_1 \approx 2$, there is a sharp increase in diffusivity at higher penetrant concentrations. The implications of this behavior are discussed later as this simple, exponential dependence is a simplification of the free volume theory. One expects an increase in penetrant diffusivity typically of 1 or 2 orders of magnitude between the initial and final phases of the swellable polymer. This corresponds to β_1 values of 2.30 and 3.91, respectively.

An increase in β_1 delays the increase in penetrant diffusivity D_1 until higher penetrant concentrations are attained. An increasing diffusivity offsets the sorption rate retarding at late times due to a flatter concentration gradient. This extends the overall sorption process a great deal since the system starts with a very low diffusivity. The extension in sorption time naturally implies a decrease in the front velocity. Therefore, the slab expands to a greater thickness as relatively more time is spent swelling in one dimension. High values of β_1 also cause a steep concentration gradient as the

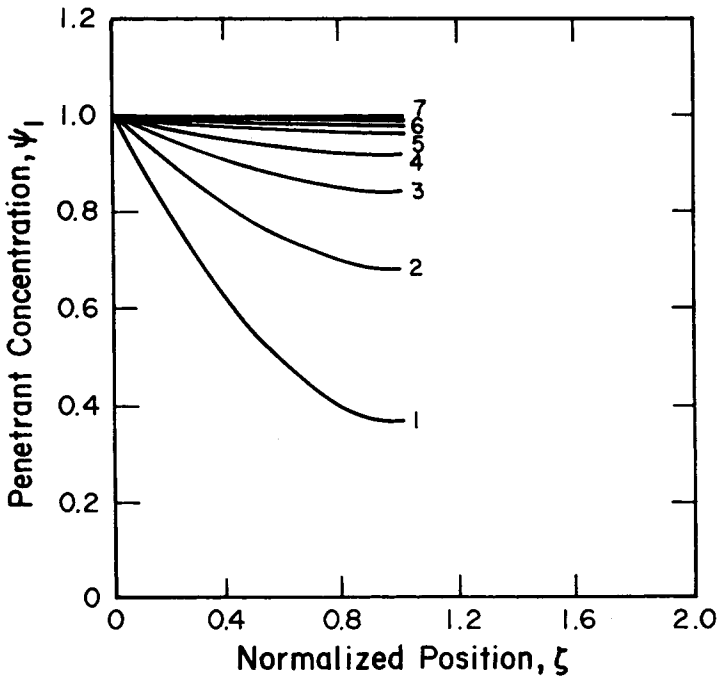


Fig. 2. Penetrant concentration profile for the case of constant solute and penetrant diffusivities and constant volume with $\beta_1 = \beta_3 = \phi_{eq} = 0$, and $D_{3s}/D_{1s} = 0.1$. The origin is taken as the left edge of the system and the profile shows the left half of the slab. Penetrant profile history shown for dimensionless times: 0.05 (1), 0.10 (2), 0.15 (3), 0.20 (4), 0.25 (5), 0.30 (6), 0.35 (7).

diffusion is retarded. Figure 2 shows a smooth penetrant concentration profile at low values of β_1, and Figure 3 shows the concentration profile under the same conditions with higher values of β_1. In these figures, the left side of the diagram represents the origin and the system expands to the right during swelling. A comparison of these two figures clearly illustrates that the sorption rate decreases. At any common position and time, the concentration corresponding to a diffusion coefficient with a high value of β_1 is lower than for a penetrant diffusion coefficient with a small value of β_1.

The kinetics of solute release is sensitive to the value of β_3. The solute diffusivity increases two to three orders of magnitude between the dry and fully swollen polymer states. This corresponds to values of β_3 of 4.61 and 6.91, respectively.

The effect of β_3 is apparent in the swelling interface number model analysis. Equations (24) and (26) indicate that an increase in β_3 decreases the swelling interface number. Increasing β_3 increases the delay in solute release until higher penetrant concentrations are attained, similar to the effect of β_1 on the penetrant diffusivity.

Although the penetrant activity is coupled to the solute diffusivity, there is no solute activity coupling of the penetrant sorption. Thus, the value of β_3 has no effect on either the penetrant sorption kinetics, system thickness, or the swelling front velocity. This is a weakness of this model since the solute activity and volume fraction are negligible at only low solute loadings.

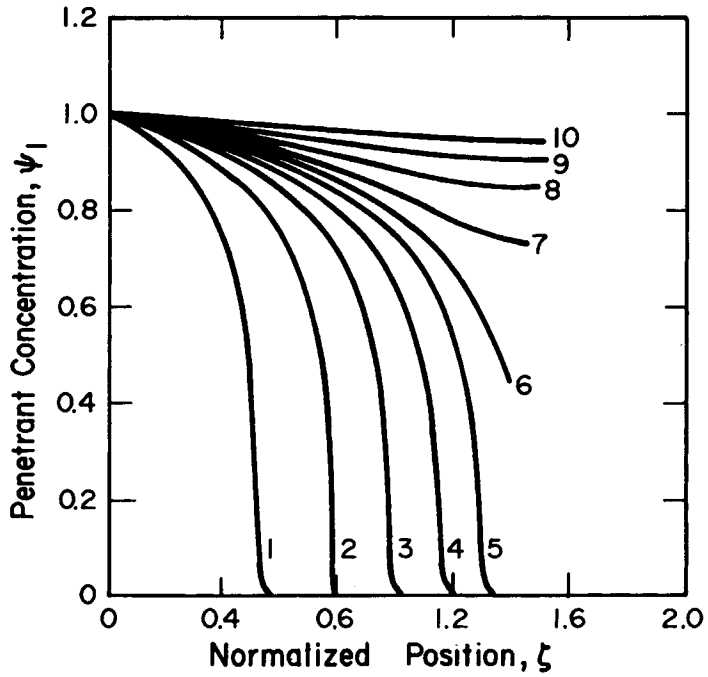


Fig. 3. Penetrant concentration profiles for the case of concentration-dependent diffusivities, $\beta_1 = 6.91$, $\beta_3 = 4.61$. Nonconstant volume, $\phi_{eq} = 0.4$, $\phi_g = 0.3$, and Deborah number, De = 0.1. The origin is taken as the left edge of the system and the profile shows the left half of the slab. Penetrant profile history shown for times: 0.05 (1), 0.10 (2), 0.15 (3), 0.20 (4), 0.25 (5), 0.30 (6), 0.35 (7), 0.40 (8), 0.45 (9), 0.50 (10).

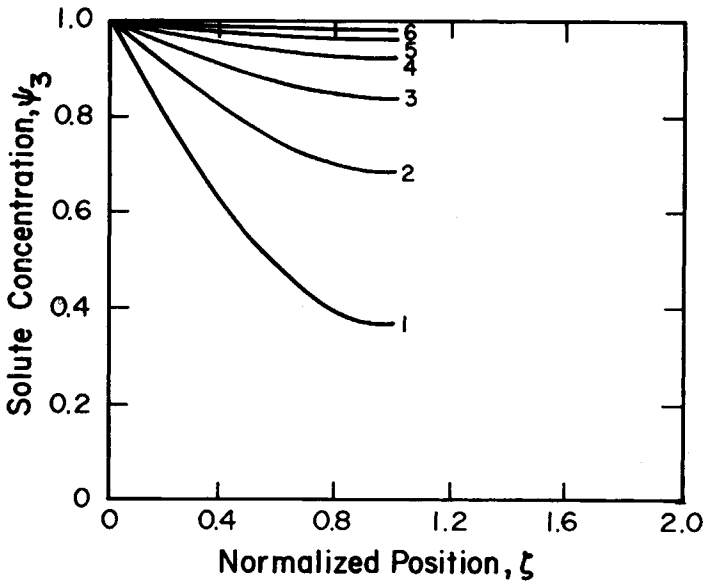


Fig. 4. Solute concentration profile for the case of constant solute and penetrant diffusivities and constant volume with $\beta_1 = \beta_3 = \phi_{eq} = 0$, and $D_{3s}/D_{1s} = 0.1$. The origin is taken as the left edge of the system and the profile shows the left half of the slab. Penetrant profile history shown for dimensionless times: 0.05 (1), 0.10 (2), 0.15 (3), 0.20 (4), 0.25 (5), 0.30 (6), 0.35 (7).

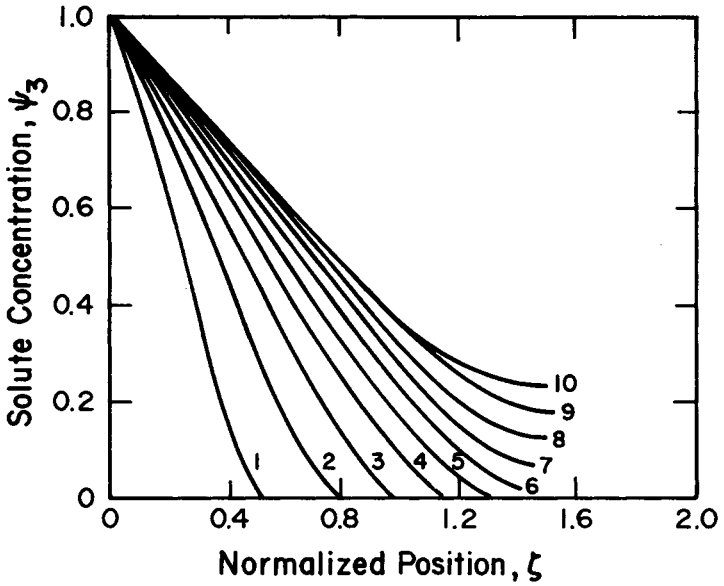


Fig. 5. Solute concentration profiles for the case of concentration-dependent diffusivities, $\beta_1 = 6.91$, $\beta = 4.61$. Nonconstant volume, $\phi_{eq} = 0.4$, $\phi_g = 0.3$, and Deborah number, De = 0.1. The origin is taken as the left edge of the system and the profile shows the left half of the slab. Penetrant profile history shown for dimensionless times: 0.05 (1), 0.10 (2), 0.15 (3), 0.20 (4), 0.25 (5), 0.30 (6), 0.35 (7), 0.40 (8), 0.45 (9), 0.50 (10).

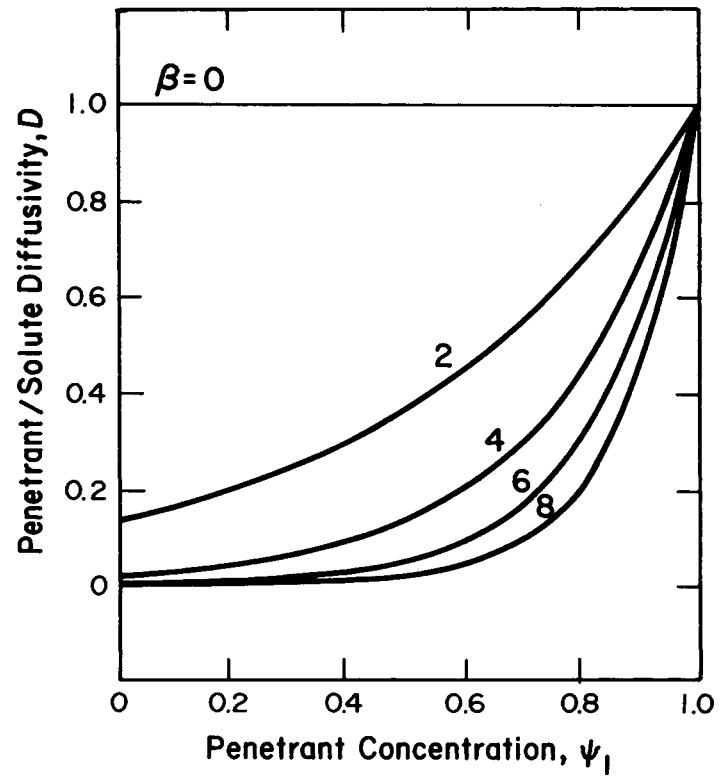


Fig. 6. Penetrant and solute diffusivity as functions of penetrant concentration for $\beta_1 = 0, 2, 4, 6, 8$.

The value of equilibrium penetrant value fraction, ϕ_g, reflects penetrant–polymer thermodynamic compatibility and the proximity of the experimental temperature to the glass transition temperature. Small values of ϕ_g (e.g., $0.01 \lesssim \phi_g \lesssim 0.2$) imply facile plasticization and macromolecular lability.

An increase in the value of ϕ_g extends the time period during which the system expands in one dimension. If macromolecular relaxations are relatively fast, the one-dimensional swelling elongates the system to a greater extent than would isotropic, three-dimensional swelling. The polymer thickness decreases when the symmetric swelling interfaces meet at the center of the sample. This volume change effectively compresses the penetrant and solute concentration gradients causing accelerations in sorption and release. If the relaxations are not very fast, this acceleration can become complementary to the retardation of solute release rate and produce portions of the release curve which are roughly linear with time. Relatively slower macromolecular relaxations inhibit the rate at which the sample elongates as it swells. The change in penetrant sorption is subtle if either the increase in diffusivity has already allowed the transport to near completion, for instance, at high β_1 and long times, or the system collapses relatively early in the sorption process, such as at low ϕ_g. The effect becomes more evident when the system collapses midway during the penetrant sorption.

An increase in the value of ϕ_g has little effect on the swelling interface velocity. Although the solute diffusivity is a function of penetrant concentration, it is not a function of the equilibrium phase transition concentration. A pronounced effect is observable on the swelling interface number. An increase in ϕ_g delays the presence of the rubbery phase until higher penetrant concentrations are attained. Since the penetrant contributes free volume to the sample, the average solute diffusivity in the rubbery phase is increased. The net effect is a decrease in the swelling interface number with an increase in ϕ_g.

An indication of the polymer's thermodynamic compatibility with the penetrant is the value of the equilibrium volume fraction of penetrant, ϕ_{eq}. The value of ϕ_{eq} determines the extent of swelling and thickness change. An increase in the value of ϕ_{eq} increases the thickness in both the isotropic and anisotropic swelling processes (see Table I).

The value of ϕ_{eq} has a prominent effect on the kinetics of penetrant sorption. Increasing system thickness during swelling extends the overall penetrant sorption and solute release as the concentration gradient is reduced. Finally, increase of both swelling front velocity and rubbery region thickness cause an increase in the swelling interface number and order of release.

A weakness of this model is that it neglects the volume fraction of the solute. Thus the model allows the three-component system to overexpand. This effect is significant at loadings greater than probably 15% vol/vol. Inclusion of this consideration would require the addition of yet another parameter, the solute loading volume fraction, $\phi_{3,d}$.

Unidirectional coupling between the penetrant sorption and solute release kinetics occurs may be expressed by the ratio of the solute to the penetrant diffusivities in the equilibrium swollen polymer, $\hat{D}$. This constant sets the relative time scale between the two processes (see Table I). Since the model excludes coupling between the solute release kinetics and the penetrant

sorption kinetics, the value of $\hat{D}$ has no effect on either the system thickness or the swelling front velocity.

Relaxation-controlled volume expansion has been incorporated in the model to investigate the experimentally observed anomalous transport behavior. The relaxation-controlled volume expansion theory used in this model is reminiscent of the Kelvin-Voigt constitutive relation[24] for stress-relaxation experiments. Although a single characteristic relaxation time has been employed, this restriction is by no means necessary. The Kelvin-Voigt had been originally utilized for describing time-dependent, macromolecular resistance to displacements induced in creep experiments. This treatment implies similar time-dependent, macromolecular resistance to the volumetric swelling induced by the incorporation of penetrant. In addition, the local elongation has been used to distinguish the dynamic motion of the swelling interface.

It should be pointed out that the characteristic relaxation time, λ, is treated rigorously as both time- and penetrant-concentration dependent.[24] Thus the Deborah number might be more appropriately treated as an instantaneous quantity.[25] Relaxation-controlled volume expansion during solvent penetration has not been investigated with a similar model; for now, we are interested in the simple case where it is constant. Small values of De, such as $\lesssim 10^{-4}$, imply fast macromolecular rearrangements, low elongational resistance. This results in fast polymer and swelling interface front velocities and a sharp thickness collapse as the glassy core vanishes. Larger values of De, such as $10^{-4} \lesssim \mathrm{De} \lesssim 0.5$, result in more gradual changes in elongation and possess the characteristic exponential-type thickness collapse[25,26] when the glassy core vanishes.

Increasing values of the Deborah number lead to a delay of the formation and the velocity of the swelling interface and thus result in a smaller instantaneous swelling interface number (see Table I). This is suspected to be somewhat of an artificial effect since the penetrant and solute diffusivities may not correctly express the actual free volume in the modeled polymer, that is, the local solute diffusivity should possess a dependence on the local polymer (glassy/rubbery) phase. Larger values of De may erroneously result in faster solute release and penetrant sorption rates since the concentration gradient is not diminished by elongation of the system.

CONCLUSIONS

A new model was developed to describe penetrant transport through and solute release from continuously swelling polymers simultaneously exhibiting a glassy/rubbery phase transition at a moving boundary. The model utilizes a Fickian mechanism for a component flux where the diffusivity incorporates a simplification of the phenomenological free volume theory. A constitutive equation describes volume expansion which is governed by macromolecular relaxations. The model describes several experimentally observed phenomena in polymer swelling, penetrant sorption, and solute release. Among the most significant characteristics of this model are its ability to describe the changes in system shape and portions of penetrant sorption and solute release where the rates are independent of time, as observed experimentally.

Although the model requires seven parameters for a solution, each parameter has well-established physical importance and could be determined from independent experiments. The simplification of the free volume theory used to describe the concentration-dependent diffusivities has resulted in the introduction of lumped parameters β_1 and β_3. These parameters can be measured by spectroscopic techniques.[18] Future improvements in this model can be easily incorporated by using the more rigorous free volume theory at the expense of increased computational effort.

NOTATION

c Concentration
d Dimensionality of swelling
De Diffusional Deborah number
D Diffusion coefficient
$\bar{D}$ Average diffusion coefficient, as defined by equation (25)
$\hat{D}$ Normalized solute diffusivity
G Stress-relaxation modulus
L_o Initial thickness
M_t Instantaneous mass
M_∞ Asymptotic mass at infinite time
Sw Swelling Interface number
t Time
x Position

Greek Letters

β Parameter describing the penetrant concentration dependence of a diffusion coefficient, as described in Eqs. (15) and (16)
δ' Initial sample thickness
δ Rubbers region thickness
ζ Dimensionless position
θ Characteristic diffusion time
λ Characteristic relaxation time
τ Dimensionless time
v Swelling interface velocity
ϕ Volume fraction
ψ Dimensionless concentration

Subscripts

d Quantity at an initial, loading condition
eq Quantity at an equilibrium state
g Quantity at the glassy/rubbery transition
o Initial quantity
s Equilibrium, swollen state
τ Instantaneous quantity
1 Penetrant or solvent species
2 Polymer species
3 Solute species

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