Solvent transport in spherical polymer–penetrant systems

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Abstract

This paper studies the transport phenomenon of solvent–penetrant systems in spherical glassy polymers. This problem involves a moving interface between a glassy region and rubbery region, the solution of which has traditionally proven very difficult. In this paper, the perturbation method is used for the complete time history of the penetrant front for a small range of perturbation control parameter \( \epsilon \). Then, a local similarity numerical simulation is used to expand the results for a large range of \( \epsilon \). Results reveal that interface velocity near time \( t = 0 \) is constant regardless of sphere dimensions, and that the interface velocity decreases after its initial constant phase, accelerating again as the interface position approaches the center of the sphere. With the proposed technique, the penetration times for different radii can be predicted. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

When a glassy polymer is exposed to a penetrant solvent, which can be gaseous or liquid, the latter diffuses into the former. An interface forms between the glassy-region and the rubbery-region, and this glass/rubber (GR) interface moves through the polymer. In the pioneering work of Alfrey, Gurnee, and Lloyd (1966), it was pointed out that the motion of the penetrant front proceeds according to time laws considerably different from classical Fickian relaxation. According to the type of polymer, the type of penetrant and the ambient conditions, different theories or equations of motion are needed for good description of the diffusion behavior occurring in individual polymer–penetrant systems.

For some polymer–penetrant systems, however, relatively slow molecular relaxation occurs only at or near the GR interface, while instantaneous Fickian diffusions can be considered in both glassy and rubbery regions. In this class of problems, the motion of the interface is dominated by a local driving force arising from solvent concentration differences. Experimental observations and data regarding the phenomenology relating to the local kinetics of the penetrant front can be found in Bagley and Long (1955), Hopfenberg, Holley, and Stannett (1969), Baird, Hopfenberg, and Stannett (1971) and Hopfenberg, Nicolais, and Drioli (1976). Astarita and Joshi (1978), Astarita and Sarti (1978) and Thomas and Windle (1982) have considered certain problems involving solvents in sorption and permeation processes in which the surface of the polymer is maintained at constant penetrant concentration. On the other hand, Cohen and Goodhart (1987) studied the problem of a polymer exposed to a finite amount of penetrant which becomes used up. Their results showed that the position of the penetrant front versus time undergoes a long smooth transition from standard Fickian \( t^{1/2} \) behavior to exponential time decay and a final equilibrium position is attained when the penetrant solvent is exhausted. Later Cohen and Erneux (1988) included the sorption of a constant reservoir of solvent and found that there is a transition of the penetrant front from initial \( t^{1/2} \) behavior (zero order or Case II diffusion) to long time \( t^{1/2} \) behavior (Fickian diffusion).

Cohen and Erneux (1988) analytically contributed the asymptotic of the interfacial position for the limit conditions of time being approximately zero and infinity. They also contributed the complete time history for small values of control parameter \( \epsilon \), which is a function of the
difference between the constant reservoir concentration and the threshold concentration. However, if asymptotic solution is no longer the main concern, solution of the moving boundary problem as Cohen and Erneux (1988) have treated it as extremely difficult or even impossible to achieve analytically. A numerical technique therefore may become the only approach for solving the problem when ε and time are not constrained to limit conditions.

This work, however, studies the transport phenomenon from an inward spherical diffusion standpoint. The perturbation method and local similarity numerical treatment are employed to investigate the complete time history of penetrant front movement. The perturbation method is restricted to the validation of small control parameter values, while numerical simulation can extend the solution to large values of ε. The history of penetrant front and the penetration time will be considered for different values of ε and radius.

2. Mathematical model of spherical polymer–penetrant system

Consider the one-dimensional spherical configuration shown in Fig. 1. The penetrant concentration within the spherical body \( R(t) < r < R_f \) is denoted by \( C \). \( C_0 \) is the solubility of the solvent in the polymer. The GR interface located at \( r = R(t) \) separates the rubbery region where the solvent concentration is high from the glassy region where the solvent concentration is almost zero. The diffusivity in the glassy region is neglected and assumed zero, while in the rubbery region, the diffusivity \( D \) of the polymer is assumed to be constant. The problem is formulated as a one-dimensional spherical moving boundary problem for the concentration \( C(r,t) \) of the penetrant and the position \( r(t) \) of the interface:

\[
\frac{\partial C}{\partial t} = D\left(\frac{1}{r} \frac{\partial^2 (rC)}{\partial r^2}\right), \quad R(t) < r < R_f, \tag{1}
\]

\[
C = C_0 > C^* \quad \text{at} \quad r = R_f, \tag{2}
\]

\[
(C + K_1) \frac{dR}{dt} = -D \frac{\partial C}{\partial r} \quad \text{at} \quad r = R(t), \tag{3}
\]

\[
\frac{dR}{dt} = -k_1(C - C^*)^n \quad \text{at} \quad r = R(t), \tag{4}
\]

\[
R(0) = R_f, \tag{5}
\]

where \( k_1, K, D, C^*, \) and \( C_0 \) are constant parameters. Eq. (1) is Fick’s law for a one-dimensional system with spherical coordinates, and Eq. (2) is the associated boundary condition at the surface. Eq. (3) describes the mass balance at the moving interface. Eq. (4) is the mathematical expression of the local kinetics driving the surface at some finite rate, as proposed by Cohen and Erneux (1988). The parameters \( K, k_1, \) and \( n \) are phenomenological quantities which can be obtained from experimental observations.

A scaling system is introduced to nondimensionalize the model equations (1)–(5), via

\[
t^* = \frac{t}{\alpha}, \quad u = \frac{C - C^*}{C_0 - C^*},
\]

\[
r^* = \frac{r}{\beta}, \quad R^*(t) = \frac{R(t)}{\beta}, \quad R_f = \frac{R_f}{\beta}, \tag{6}
\]

where

\[
\alpha = \frac{D(C_0 - C^*)^{1 - 2n}}{Ck_1^2}, \quad \beta = \frac{D(C_0 - C^*)^{1 - n}}{Ck_1}
\]

and

\[
\bar{C} = C^* + K.
\]

The reduced dimensionless model equations are

\[
\frac{\partial u}{\partial t} = \varepsilon^{-1} \left(\frac{1}{r} \frac{\partial^2 (ru)}{\partial r^2}\right), \quad R(t) < r < R_f, \tag{7}
\]

\[
u = 1 \quad \text{at} \quad r = R_f, \tag{8}
\]

\[
(1 + \alpha u)R^* = -\frac{\partial u}{\partial r} \quad \text{at} \quad r = R(t), \tag{9}
\]

\[
R^* = -u^\alpha \quad \text{at} \quad r = R(t), \tag{10}
\]

\[
R(0) = R_f, \tag{11}
\]

where \( \varepsilon \) is a control parameter defined by

\[
\varepsilon = \frac{C_0 - C^*}{C}.
\]

Fig. 1. The spherical configuration for the inward solvent–penetrant system.
The parameter $C^*$ is the threshold concentration for penetrative movement of the solvent, so parameter $\varepsilon$ must be greater than zero to assure movement of the interface. It should be noted that the star sign of the dimensionless quantities in Eqs. (7)–(11) has been omitted for convenience.

3. Solution of the perturbation method

Exact solution of the moving boundary problem (7)–(11) is very difficult to find analytically. Thus, an approximate solution of the system is sought. The perturbation technique is adopted for the limit $\varepsilon \to 0$ to study the complete time evolution of the penetrant front. Solution of these equations is sought in the form

$$u(r,t,\varepsilon) = u_0(r,t) + \varepsilon u_1(r,t) \cdots$$

and

$$R(t, \varepsilon) = R_0(t) + \varepsilon R_1(t) \cdots$$

Upon substituting (12) and (13) into (7)–(11) and equating like powers of $\varepsilon$, we can obtain the following problem for $R_0$ and $u_0$:

$$\left( \frac{1}{r} \frac{\partial^2 (ru_0)}{\partial r^2} \right) = 0, \quad R_0(t) < r < R_f,$$  \hspace{1cm} (14)

$$u_0 = 1 \quad \text{at} \quad r = R_f,$$  \hspace{1cm} (15)

$$R_0 = - \frac{\partial u_0}{\partial r}, \quad \text{at} \quad r = R_0(t),$$  \hspace{1cm} (16)

$$R_0^n = - u_0^n \quad \text{at} \quad r = R_0(t),$$  \hspace{1cm} (17)

$$R_0(0) = R_f.$$  \hspace{1cm} (18)

The solution of Eqs. (14) and (15) is given by

$$u_0(r,t) = 1 + A(t) \left( \frac{1}{r} - \frac{1}{R_f} \right)$$  \hspace{1cm} (19)

where $A(t)$ is an arbitrary function of $t$ to be determined by Eqs. (16)–(18). From Eqs. (16) and (17),

$$R_0^n = \left[ 1 + A(t) \left( \frac{1}{R_0} - \frac{1}{R_f} \right) \right]^n,$$  \hspace{1cm} (20)

$$R_0 = \frac{A(t)}{R_0}.$$  \hspace{1cm} (21)

Eliminating $A(t)$, we can find the ordinary differential equation for $R_0$:

$$R_0^n = - \left[ 1 + R^2 \left( \frac{1}{R_0} - \frac{1}{R_f} \right) \right]^n.$$  \hspace{1cm} (22)

The position of the penetrant front can be obtained by numerical integration using $R_0(0) = R_f$. For the case $n = 1$, we find

$$R_0 - R_f + \frac{1}{4} (R_0^2 - R_f^2) - \frac{1}{4} (R_0^2 - R_f^2) / R_0 = - t$$  \hspace{1cm} (23)

which can be solved by Newton–Rafson iteration. For time approximately zero, $R_0 \to R_f$, $(R_f - R) \sim t$ and $R'_0 = - 1$, indicating that the GR interface moves through the polymer at a velocity which is constant near time $t = 0$ for all dimensions of the sphere, and is consistent with the planar case.

4. Local similarity solution

This section proposes a numerical method for solving the moving boundary problem (7)–(11). A local similarity solution is applied in the form

$$u(r,t) = \frac{X(t)}{r} \text{erf} \left( \frac{R_f - r}{\sqrt{4e^{-1}t}} \right) + \frac{R_f}{r}$$  \hspace{1cm} (24)

which automatically satisfies the boundary condition (8). Expression (24) is an exact solution of diffusion equation (7) only if $X$ is constant for all times. Unfortunately, in the moving boundary problem under consideration, parameter $X$ is normally not constant. However, expression (24) does work in a numerical treatment in which $X(t)$ is considered to be a piece-wise constant during an interval $(t_{i-1}, t_i)$. The remaining boundary conditions (9) and (10) then become

$$\left\{ 1 + \varepsilon \left[ X \text{erf} \left( \frac{R_f - R}{\sqrt{4e^{-1}t}} \right) + R_f \right] \right\}$$

$$\times \left[ \frac{1}{R} \left( X \text{erf} \left( \frac{R_f - R}{\sqrt{4e^{-1}t}} \right) + R_f \right) \right]^n$$

$$+ \frac{1}{R^2} \left( X \text{erf} \left( \frac{R_f - R}{\sqrt{4e^{-1}t}} \right) + R_f \right)$$

$$+ \frac{X}{2} \frac{1}{\sqrt{\pi} \sqrt{4e^{-1}t}} \exp \left( - \frac{(R_f - R)^2}{4e^{-1}t} \right) = 0$$  \hspace{1cm} (25)

and

$$\frac{dR}{dt} = - \left[ \frac{1}{R} \left( X \text{erf} \left( \frac{R_f - R}{\sqrt{4e^{-1}t}} \right) + R_f \right) \right]^n.$$  \hspace{1cm} (26)

The strategy of the calculation is to solve parameter $X$ from Eq. (25) and then obtain the interfacial moving rate from Eq. (26), but this can be done only after the interface position $R$ is found. To determine the history of the interfacial position $R$, in the analysis, we will numerically integrate

$$R_i = R_{i-1} + \frac{dR_{i-1}}{dt}(t_i - t_{i-1}), \quad i = 1, 2, \ldots$$  \hspace{1cm} (27)
5. Results and discussion

As seen above, the perturbation method provides the approximate solution of the solvent penetration system inside a sphere. $\varepsilon$ is the small parameter required by the perturbation method and is proportional to the deviation $C_0 - C^*$, where $C_0$ is the solubility in the swollen phase corresponding to the imposed external activity of solvent, and $C^*$ the swollen-side threshold concentration for swelling. The zero-order term in the asymptotic expansion represents a quasi-steady-state approximate solution. The results show that sphere radius does not contribute to the interface velocity when time is approximately zero. However, the asymptotic solution is no longer useful with large values of $\varepsilon$. Therefore, numerical methods are used to provide approximate solutions to the problem, solutions not constrained to the limit conditions of the perturbation method.

From Fig. 2 it can be seen that when the radial dimension of the sphere, $R_f$, is very large, both asymptotic and numerical solutions approach the planar case as studied by Cohen and Erneux (1988) and that the front location decreases more rapidly when $R_f$ is smaller. The two approaches are quite close when $\varepsilon$ is small. The interface penetration velocities with different sphere dimensions are shown in Fig. 3. By numerical simulation, the velocity of the GR interface over the initial period of penetration is a constant, regardless of the sphere’s dimensions. This result is consistent with perturbation analysis. As time proceeds, the penetration velocity slows. However, as the interface approaches the center, the penetration velocity increases. Generally speaking, the GR interface penetrates more rapidly for spheres of small radius.

For various $\varepsilon$ and $R_f = 5$, the GR interface time history is shown in Fig. 4, while the penetration velocity time history is shown in Fig. 5. It can be seen that when
$$e$$ is small, e.g. $$e = 0.01$$, numerical solution of the interface position is coincident with the perturbation solution, as marked by empty circles in Fig. 4. If $$e$$ increases, it decreases the penetration velocity. As $$e \to 0$$, we note that inward interface velocity remains constant for longer periods of time. Hence, it takes more time for the GR front to reach the center of sphere with large $$e$$. From this figure, the advantage of the numerical treatment can be easily seen since finite values of $$e$$ can be chosen in the simulation, unlike asymptotic investigations in which only small $$e$$ may be used for describing the complete time history of the interface position. Moreover, the perturbation solution, in this paper, cannot provide the information of influence of the control parameter $$e$$ on the movement of GR interface.

The effect of changing $$n$$ is shown in Figs. 6 and 7. As $$n \to 0$$, the inward interface velocity remains constant for longer periods of time, and it shortens the time for the
GR front to reach the center of the sphere. Here, we define penetration time as the time needed for the penetrant front to reach the center of the sphere. At penetration time, the glassy region vanishes. Figs. 8 and 9 portray penetration time with respect to the effects of $e$ and $n$. It can be seen that large $e$ and $n$ result in large penetration time, with results that can be predicted quantitatively.

6. Conclusions

In the present work, solvent penetration phenomena for inward spherical diffusion are considered. The perturbation method and a local similarity numerical treatment are used to investigate the complete time history of penetrant front movement. The perturbation method is restricted to the validation of a small control parameter, and can only predict the phenomena qualitatively. Numerical simulation extends the solution to large values of the system control parameter.

Asymptotic solutions valid for small values of $e$ are studied in Section 2. For the initial penetration period, it is found that the GR interface moves through the polymer with a constant velocity regardless of the radius of the sphere, consistent with the planar case. In Section 3, the local similarity simulation is introduced. The complete time history of the diffusion system is divided into a finite number of time steps, in which the diffusion system of each step is treated as a fixed boundary problem and can be solved step by step with numerical integration.

For small values of parameter $e$, the numerical results are successfully reduced to those obtained by the perturbation method. The advantage of the numerical treatment is that results for all values of $e$ can be reached precisely, provided time steps are adequately small. The results show that the inward interface velocity remains constant for longer periods of time as $e$ and $n$ approach zero. Therefore, the penetration time is shortened as $e \to 0$ or $n \to 0$.

References