TRAPPING SKINNING IN POLYMERS: THEORETICAL PREDICTIONS

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During the desorption of certain saturated polymer films, a thin skin of glassy polymer can form at the exposed surface. Not only does this inhibit desorption, but also trapping skinning, in which an increase in the desorption driving force decreases the accumulated flux, can occur. These behaviors cannot be described by a simple Fickian flux. A theoretical framework is presented for modeling such a system. It is shown that though increasing the driving force will increase the instantaneous flux, the time of accumulation will decrease, thus reducing the accumulated flux. In addition, the model is shown to exhibit sharp fronts moving initially with constant speed, another distinctive feature of non-Fickian polymer-penetrant systems.

Keywords: Desorption; non-Fickian diffusion; polymer-penetrant systems; skinning; trapping skinning

INTRODUCTION

One unusual feature of certain polymer-penetrant systems is a change of state in the polymer from a *rubbery* state when the polymer is nearly saturated to a *glassy* state when the polymer is nearly dry. During the desorption of such a saturated film or fiber, often a glassy region, or skin, develops at the exposed surface. Since the polymer is now in two states – the glassy skin and the deeper rubbery material – this phenomenon is called *literal skinning* (Cairncross and Durning, 1996; Cairncross et al., 1992; Crank, 1950; Crank and Park, 1951). Due to the smaller diffusion coefficient

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in the glassy region, this skin will slow the desorption process (Powers and Collier, 1990).

This glassy skin can be used as a natural barrier to create more effective protective clothing, equipment, or sealants (Vieth, 1991; Vrentas et al., 1975). Also, this skinning phenomenon can be desirable for such processes as membrane production by phase inversion (Anderson and Ullman, 1973) or spray drying operations (Charlesworth and Marshall, 1960). However, polymer skinning is generally undesirable in coating processes due to nonuniformities in the polymer coating and a decrease in drying rates (Cairncross and Durning, 1996).

Trapping skinning is an anomalous special case of the skinning effect in which an increase in the force driving the desorption will actually decrease the accumulated flux through the boundary (Cairncross and Durning, 1996; Powers and Collier, 1990). Crank (1950) and Crank and Park (1951) showed that this behavior cannot be fully explained by the lower Fickian diffusion coefficient in the glassy region. Thus, other effects, such as those due to viscoelasticity, must be included. Though the dynamics of these systems are incredibly complex, most agree that one dominant factor is a viscoelastic stress in the polymer, which is related to the polymer's relaxation time. In certain polymer-penetrant systems, this stress is as important to the transport process as the well-understood Fickian dynamics (Frisch, 1980). In the glassy region, the relaxation time is finite, so the stress is an important effect. In the rubbery region, the relaxation time is nearly instantaneous; hence, the memory effect is not as important there (Frisch, 1980; Vieth, 1991).

In this paper, we outline a study of a previously-derived model (for instance, see Edwards and Cohen, 1995b, 1995c) to explain this unusual behavior. We track two important measurable quantities: the flux of the penetrant through the exposed boundary and the dynamics of the front separating the glassy and rubbery regions. Each of these quantities is identified and related to the dimensionless parameters in the problem. These computations should provide useful information to chemical engineers who wish to verify our model experimentally and if our model is shown to be accurate, to those who wish to accommodate the skinning phenomenon in the production process.

GOVERNING EQUATIONS

Edwards (1997) presents the following dimensionless model for non-Fickian diffusion in a skinning system:

$$C_t = [D(C)C_x + \sigma_x]_x, \quad x \geq 0, \tag{1a}$$

$$\sigma_t + \frac{\beta(C)}{\beta_g}\sigma = \frac{\gamma}{\varepsilon}C + C_t, \tag{1b}$$

$$\beta(C) = \begin{cases} \beta_g, & 0 \leq C \leq C_* \text{ (glass)}, \\ \beta_r, & C_* < C \text{ (rubber)}, \end{cases} \quad \frac{\beta_g}{\beta_r} = \varepsilon, \quad 0 < \varepsilon \ll 1, \tag{2a}$$

$$D(C) = \begin{cases} D_g\varepsilon, & 0 \leq C \leq C_*, \\ D_r, & C_* < C, \end{cases} \tag{2b}$$

$$D(C)C_x(0,t) + \sigma_x(0,t) = kC(0,t), \tag{3}$$

$$(D(C_*^-) + 1)C_x(s^-(t),t) - (D(C_*^+) + 1)C_x(s^+(t),t) + \frac{(1 - \varepsilon^{-1})\sigma(s(t),t)}{s} = a\dot{s}. \tag{4}$$

Each of the variables in (1)–(4) has been scaled with respect to physically observable lengths and times. The flux, which is the negative of the bracketed quantity in (1a), arises from postulating that the chemical potential depends on both C and the non-state variable σ, which models memory effects (Edwards and Cohen, 1995b). Since (1b) is reminiscent of an evolution equation for viscoelastic stress, we refer to σ as a "stress" throughout this work. Equations (1) have been successfully used to model various types of anomalous behavior in polymer-penetrant systems (for example, see Edwards, 1996). We use a semi-infinite medium since we want to avoid considering the effects of swelling on the system.

$\beta(C)$, the inverse of the relaxation time, and $D(C)$, the molecular diffusion coefficient, have been taken to be piecewise constant. C_* is the concentration at which the rubber-glass transition occurs. Here ε is the ratio of the relaxation times, which we shall drive to zero to use as a perturbation parameter. As $\varepsilon \rightarrow 0$, we see that this enhances the difference between the two states and hence we would expect to see sharp concentration profiles near the glass-rubber interface $s(t)$. In addition, as $\varepsilon \rightarrow 0$, large differences develop between the values of β and D in the two states. Such large differences in D have been seen experimentally (Duda et al., 1982) and have been exploited in previous models of the phenomena (Hui et al., 1987b; Vieth, 1991).

These piecewise-constant forms are obviously idealizations of the true parameter dependences and other choices are certainly possible. Many authors use exponential dependence of D on C (for example, see Petropoulos and Roussis, 1978), though this form does not accurately model the inflection points often seen in the diffusion coefficient (Duda *et al.*, 1982). Our choice is motivated by the fact that in certain polymer-penetrant systems, a severe increase in D is localized about the glass-rubber interface where $C = C_*$ (Frisch, 1964, 1980; Huang and Durning, 1997; Hui *et al.*, 1987a, 1987b). In addition, the relaxation time decreases radically at the glass-rubber transition, which causes a corresponding increase in β (Frisch, 1980; Huang and Durning, 1997; Vieth, 1991). Therefore, we use the average of β and D in each state as its value throughout the state. This averaging, which yields the piecewise-constant form in (2), has produced qualitative agreement with several types of anomalous diffusion behavior (Edwards and Cohen, 1995a; Hui *et al.*, 1987b; Witelski, 1996).

Crank (1951, 1953) used such piecewise-constant forms for D to model this nonstandard behavior. The use of constant D in the glassy region has been shown to provide good qualitative descriptions of the behavior (Hopfenberg and Stannett, 1973) and excellent agreement with experimental data (Lasky *et al.*, 1988). Experimental agreement has even been obtained with a model where D is kept at the same constant value throughout *both* states (Edwards and Cohen, 1995b). Therefore, though the piecewise-constant form is only an idealization, we believe the results thus obtained have the same qualitative structure as the full physical system. More discussion of various physically appropriate forms for $D(C)$ can be found in Cohen and White (1989).

As noted by Crank (1950) and Crank and Park (1951), the lower diffusion coefficient in the glassy region is not enough to explain trapping skinning and indeed there can be significant diffusion in glassy polymers with a small diffusion coefficient (Edwards, 1995; Lasky *et al.*, 1988). Thus, viscoelastic relaxation effects must come into play. Wu and Peppas (1993) define the integral sorption Deborah number as the ratio of the diffusion rate in the rubbery region to the relaxation rate in the glassy region. In our notation,

$$De = \frac{\tilde{D}_r}{\beta_g L^2}, \tag{5}$$

where $\tilde{D}_r$ is the *dimensional* molecular diffusion coefficient in the rubbery region and L is a typical length scale. Therefore, we choose this normalization for the molecular diffusion coefficient to obtain $D_r = De$.

Since in our analysis $D_r = De = O(1)$ (in fact, the figures illustrate a case where $De = 3$), we are in the regime where anomalous diffusion can be expected.

Lastly, we note that the relative sizes of the parameters in Eqs. (1)–(4) have been chosen quite carefully. As written, every parameter in (1)–(4) but ε is an $O(1)$ quantity. These parameter sizes result from scaling the length and time variables by quantities associated with the stress in the glassy region and from assuming that the C term is dominant in (1b). Other scalings and assumptions lead to different sizes of the parameters, which lead to different balances in the equations. These alternative balances lead to more standard desorption profiles, lending credence to the theory that trapping skinning is a most unusual effect which is difficult to capture experimentally.

Initially, we set the concentration in the polymer to a uniform value of 1. To ensure that the polymer is initially rubbery, we require that $C_* < 1$. Given these conditions, the stress quickly equilibrates to a uniform value of γ on a fast time scale (Edwards, 1997). The parameter γ is a ratio measuring the relative contributions of the concentration and time-derivative terms in (1b).

Equation (3) is the standard radiation condition at the exposed edge for our augmented flux, where we assume that the exterior concentration is zero. Here the parameter k is related to parameters which affect the drying rate, such as the airflow rate in the exterior. Generally, k increases with conditions that promote drying. From (3) we see that if the boundary is dry (i.e., if a skin has formed), then there will be very little flux through the boundary and the penetrant will be trapped inside the polymer. We require continuity of concentration and stress at the moving front $s(t)$ between the two states. Equation (4) arises as a result of a Stefan-like condition imposed at the moving boundary (Edwards and Cohen, 1995c).

Lastly, we define the *accumulated flux* F:

$$F \equiv \int_0^\infty [D(C)C_x + \sigma_x](0, t)dt. \tag{6}$$

In normal desorption or literal skinning, an increase in k would increase F. However, in our model we will show that though an increase in k will increase the *instantaneous* flux, it will actually produce a *decrease* in F.

THE ACCUMULATED FLUX

The solutions in Edwards (1997) are based on singular perturbation methods using ε as the perturbation parameter. Memory effects are not

important in the rubbery state and hence the solution in this region is given by a standard Fickian-type profile:

$$C(x,\ t) = \mathrm{erf}\left(\frac{x}{2\kappa\sqrt{t}}\right) + \exp\left(\frac{kx + k^2 t}{\kappa^2}\right)\mathrm{erfc}\left(\frac{2kt + x}{2\kappa\sqrt{t}}\right), \quad \kappa^2 = D_r + \gamma.$$

$$(7)$$

It can also be shown that in this region we have

$$\sigma = \gamma C. \tag{8}$$

The Fickian-type profile continues until the concentration at the exposed edge reaches the glass-rubber transition value C_*, which occurs at a time given by

$$e^{z_*}\,\mathrm{erfc}\,\sqrt{z_*} = C_*, \quad t_* = \frac{\kappa^2 z_*}{k^2}. \tag{9}$$

From (1a) and (8) one can see that the parameter κ^2 combines the contributions to the flux from the concentration gradient and stress gradient. Note that the time needed to dry the surface to $C = C_*$ decreases with increasing k, as expected.

Note from (9) that z_* is a function of C_* only, as illustrated in Figure 1. The following asymptotic results are of interest:

$$z_* \sim \begin{cases} \dfrac{(1 - C_*)^2 \pi}{4}, & C_* \to 1, \\[3mm] \dfrac{1}{C_*^2 \pi}, & C_* \to 0. \end{cases} \tag{10}$$
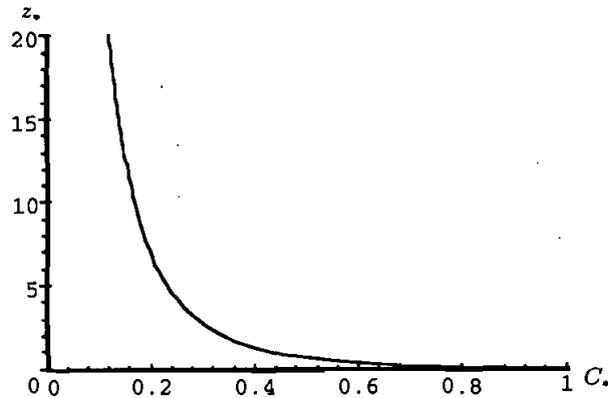

FIGURE 1 z_* vs. C_*.

Therefore, we see that if the glass-rubber transition concentration is near the saturation concentration, the polymer will very quickly transition to the glassy state. Also, if the glass-rubber transition is far from the saturation concentration, we can delay the onset of the glassy state indefinitely. This is consistent with our physical intuition for the system.

Figure 2 shows a graph of $C(x)$ vs. x. The concentration decreases monotonically with t, so the line $C = 1$ corresponds to $t = 0$ and the graph where $C(0, t) = 0.5 = C_*$ corresponds to t_*, the value of which was calculated numerically from (9). Note the standard Fickian profile. In addition, note from (8) that for the particular value of γ we have chosen, Figure 2 is also a graph of $\sigma(x)$.

In order to track F, we need to examine the concentration profile in the glassy region for $t > t_*$ and near the exposed boundary. We summarize the results in Edwards (1997). There is no stress dispersion in the glassy region and hence from (8) and continuity of stress at $s(t)$ we have

$$\sigma(x, t) = \gamma C_*, \quad x < s(t). \tag{11a}$$

Due to the finite relaxation time in the glassy region, we see from (1b) that the concentration must be small:

$$C(x, t) = \varepsilon C_*, \quad x < s(t). \tag{11b}$$

It can be seen immediately that (11b) is not C_* at the front $s(t)$ and indeed there is a sharp interior layer around the front where the solution changes very quickly. However, for the purposes of computing F, we need only Eqs. (11).
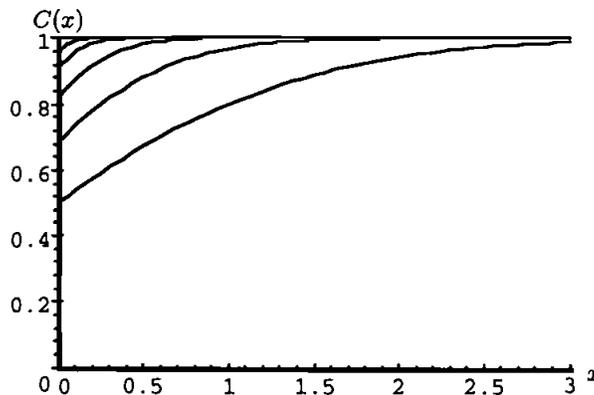

FIGURE 2 $C(x)$ and $\sigma(x)$ vs. x for $C_* = 0.5$, $\kappa = 2$, $k = 3$, $\gamma = 1$, $t_* \approx 0.262$ and $t = 0, 0.01, 0.04, 0.16, 0.64$ and t_*.

Substituting (11) into (6), we see that since ε is small, the contribution to F from desorption in the rubbery state $(0 \leq t \leq t_*)$ dominates that from desorption in the glassy state $(t > t_*)$. Camera-Roda and Sarti (1990) obtained a similar result in a case where $k \rightarrow \infty$ and the ratio of the diffusivities is large. In our model, this result can be interpreted physically by examining (1b). Due to the finite relaxation time in the glassy polymer, an $O(1)$ concentration flux through the boundary would require an $O(\varepsilon^{-1})$ stress, which is larger than the glassy polymer can support if it is not initially prestressed at such a high value.

Since the flux in only the rubbery region contributes to the leading order of our solution, we use (7) to obtain

$$F = \frac{\kappa^2}{k} \left[2\sqrt{\frac{z_*}{\pi}} - (1 - C_*) \right]. \tag{12}$$

Equation (12) deserves close scrutiny. An increase in κ will increase F, as it should since we are increasing the diffusion coefficient. However, for fixed C_*, an increase in k, which would normally increase the amount of penetrant desorbed, will actually *decrease F*. This embodies the very essence of trapping skinning (Cairncross and Durning, 1996; Powers and Collier, 1990).

How does this happen? Equation (3) shows that an increase in k will increase the *instantaneous* flux through the boundary. But from (9) we see that this increase causes the exterior surface to desorb faster, thus reducing the glass-transition time t_* at which our flux accumulation effectively ends. Therefore, there is a competition between these two effects, one which the shorter accumulation time dominates.

Lastly we consider the behavior of F as C_* takes on extremal values. Using (10), we obtain

$$F \sim \begin{cases} 0, & C_* \rightarrow 1, \\ (2\kappa^2/kC_*\pi), & C_* \rightarrow 0. \end{cases} \tag{13}$$

Therefore, we see that if the transition concentration is very near the saturation concentration, there is little time for the penetrant in the rubbery region to diffuse through the exposed surface, and hence F is small. On the other hand, if the transition concentration is low, the polymer is in the rubbery region for a long period of time and hence F becomes arbitrarily large, which it can do since we have an infinite reservoir of penetrant.

THE FRONT POSITION

The perturbation analysis needed to complete the solution of our problem is rather detailed and has been described elsewhere (Edwards, 1997). Here we wish to expand upon the physical significance of the major results. As noted earlier, our solution given by (11b) does not match one of our conditions at the front. An interior layer of width ε must be introduced to match the two solutions together. Therefore, as surmised earlier, smaller values of ε cause sharper interfaces.

Once we have introduced this layer, (4) becomes

$$C_x(s^+(t), t) = -\frac{a + C_*}{\kappa^2} \dot{s},$$

which, along with the form of the concentration in the rubbery region, implies that

$$a < -1. \tag{14}$$

This requirement indicates that a cannot be interpreted in terms of the latent heat, since in this case the phase change parameter is negative. However, a restriction of the form of (14) is not uncommon for the model Eqs. (1) (Edwards and Cohen, 1995b). Since the stress term in the flux acts to oppose front motion, we see that it is the difference of the two competing effects which is critical to the dynamics of the front. Therefore, we see that it is reasonable to assume that a could be of either sign, depending on the relative strengths of the viscoelastic and Fickian effects in a particular system.

To calculate the front motion, we must compute the solution in the rubbery region for $t > t_*$. The calculation involves a set of integral equations which can be solved asymptotically for t near t_* and for large t (Edwards, 1997). Performing the asymptotics, we see that the front position is given by

$$\dot{s}(t) \sim \frac{kC_*(t - t_*)}{|a + C_*|}, \quad t \to t_*^+, \tag{15}$$

$$s(t) \sim 2\kappa s_\infty t^{1/2}, \quad t \to \infty, \tag{16}$$

where s_∞ is given by the root of the equation

$$1 - C_*[1 - s_\infty(\text{erfc } s_\infty) \exp(s_\infty^2)\sqrt{\pi}] = |a|s_\infty(\text{erfc } s_\infty) \exp(s_\infty^2)\sqrt{\pi}. \tag{17}$$

We note that s_∞ does not depend on k. This is consistent with the observation that in a system of finite width, the steady-state skin depth does not depend appreciably on k (Anderson and Ullman, 1973).

Some discussion of the dependence of s_∞ on our parameters is appropriate. It can be shown that as C_* gets smaller, s_∞ gets smaller. This agrees with our intuition, as we expect that the front would slow as the rubber-glass transition value decreases. In addition, as a increases, the front speed increases. This is because the absolute value of the jump in the flux needed to move the front along is decreasing and hence the front should move faster.

Figure 3 shows a graph of the short- and long-time expansions of our front position $s(t)$ in the x-t plane. In addition, there is a darker curve which interpolates between the two asymptotic expansions to show how the true front might behave. Note that the front slows as time increases.

SOLUTION PROFILES

Explicit closed-form long- and short-time asymptotic solutions for the concentration and stress can be found in Edwards (1997). However, it is perhaps more instructive to glean physical insight from graphs of our solution profiles.

Figure 4 shows a graph of $C(x)$ vs. x for t near t_* and various parameters; note that (14) is satisfied. On a relatively fast time scale (note that our largest $t = t_* + 0.1$), the concentration in the glassy region decays away. This is the
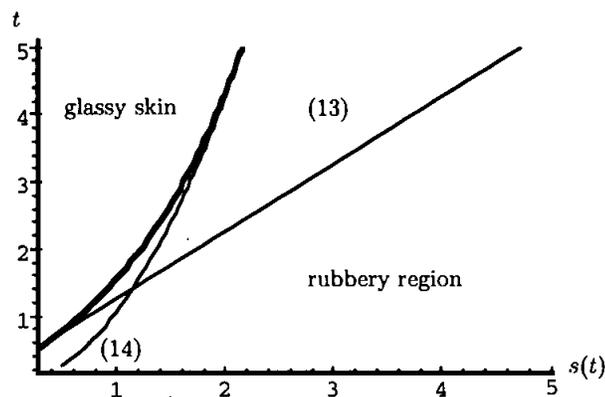

FIGURE 3   Short- and long-time asymptotes for $s(t)$ for $C_* = 0.5$, $a = -2$, $D_g = 2$, $\varepsilon = 0.01$, $\kappa = 2$, $k = 3$, $\gamma = 1$ and $t_* \approx 0.262$.
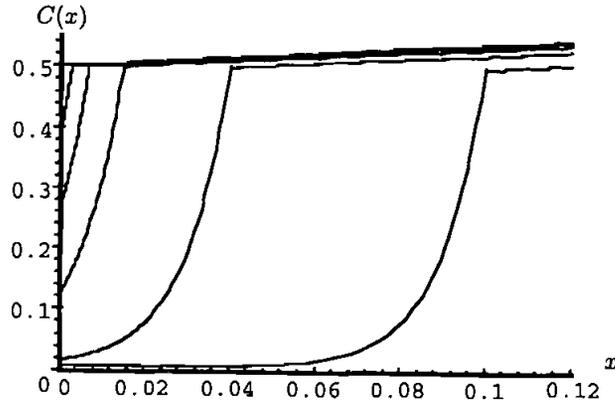
FIGURE 4 $C(x)$ vs. x for $C_* = 0.5$, $a = -2$, $D_g = 2$, $\epsilon = 0.01$, $\kappa = 2$, $k = 3$, $\gamma = 1$, $t_* \approx 0.262$
and $t - t_* = 0$, 0.003, 0.007, 0.015, 0.04 and 0.1.

mathematical manifestation of the formation of the glassy skin near the exposed surface. Note also that due to the small scale in the x-direction, our front is very sharp. This is more apparent in Figure 5, which shows a graph of $C(x)$ vs. x for the same parameters as graphed earlier and for long times. It is clear that the concentration flux through the exposed boundary is zero to the order of our approximation.

In addition, we can use (8) and (11a) to yield graphs of the stress for small and large times. Figure 6 shows $\sigma(x)$ vs. x for the same parameters and times as in Figure 4. We note that rather than decaying to zero as the
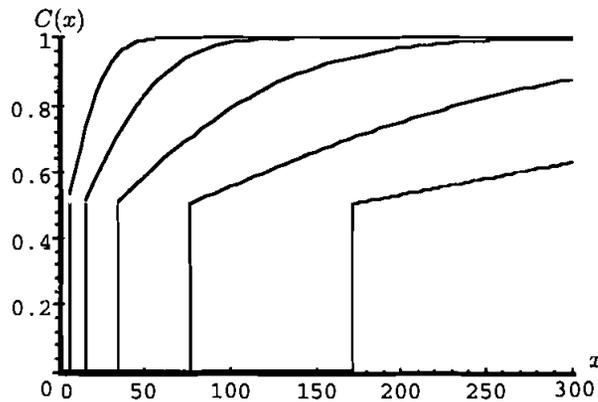

FIGURE 5 $C(x)$ vs. x for $C_* = 0.5$, $a = -2$, $D_g = 2$, $\epsilon = 0.01$, $\kappa = 2$, $k = 3$, $\gamma = 1$ and $t = 50$, 250, 1250, 6250 and 31250.
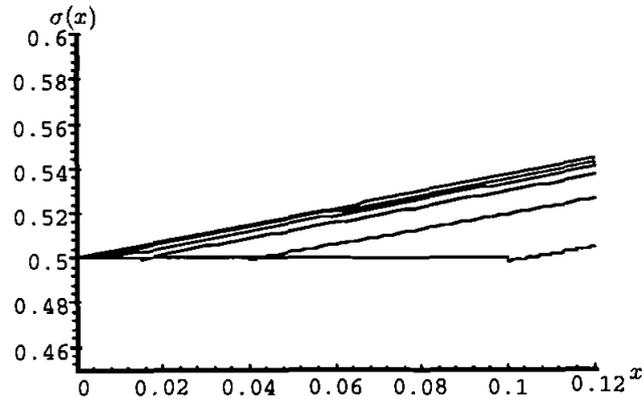
FIGURE 6 $\sigma(x)$ vs. x for $C_* = 0.5$, $a = -2$, $D_g = 2$, $\varepsilon = 0.01$, $\kappa = 2$, $k = 3$, $\gamma = 1$, $t_* \approx 0.262$ and $t - t_* \equiv u = 0$, 0.003, 0.007, 0.015, 0.04 and 0.1.

concentration did, the stress in the glassy region remains at a constant value γ before making a smooth transition to the rubbery region. Figure 7 shows a graph of $\sigma(x)$ vs. x for the same times and parameters as in Figure 5. We once again note that the rubbery portion of the graph is the same as that for the concentration since $\gamma = 1$. We see that the stress in the glassy region remains at a constant value, which smoothly transitions in a Fickian way to the fully stressed polymer when $x \rightarrow \infty$.
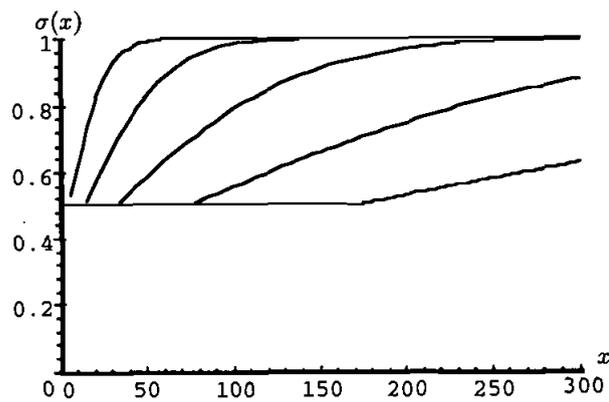

FIGURE 7 $\sigma(x)$ vs. x for $C_* = 0.5$, $a = -2$, $D_g = 2$, $\varepsilon = 0.01$, $\kappa = 2$, $k = 3$, $\gamma = 1$ and $t = 50$, 250, 1250, 6250 and 31250.

CONCLUSIONS

Trapping skinning is a counterintuitive phenomenon: an increase in k, which usually increases the total driving force for desorption, will actually decrease the amount of penetrant desorbed. A glassy skin forms at the exposed surface; such a skin slows desorption since the molecular diffusion coefficient is smaller there (Cairncross and Durning, 1996; Cairncross et al., 1992; Powers and Collier, 1990). However, the lower diffusion coefficient cannot fully explain such behavior; rather, nonlinear viscoelastic effects must also be considered (Cairncross and Durning, 1996; Crank, 1950; Powers and Collier, 1990).

A mathematical model was presented to capture this behavior. Though the model necessarily simplified the complicated dynamics of the full system, the solutions thus obtained did qualitatively match the phenomenon of trapping skinning. Since the polymer is initially saturated, for a finite amount of time the polymer remains totally in the rubbery state. Because memory effects are unimportant in the rubbery state (Vieth, 1991), the concentration flux during this interval behaves in a purely Fickian way.

Once the concentration at the boundary reaches C_*, the glass-rubber transition concentration, the character of the solution changes drastically. An interior layer around $x = s(t)$ forms a sharp interface between the rubbery and glassy regions. This sharp front initially moves with constant speed: behavior which is reminiscent of case II diffusion in sorption experiments (Thomas and Windle, 1978). Thus, we see that in this interval, Fickian dynamics are subdominant.

To determine whether or not there is trapping skinning, we examine the accumulated flux F through the boundary. Since the concentration in the glassy polymer is nearly zero, the dominant contribution to F is from the rubbery region. As expected, the instantaneous flux through the boundary increases when k, which is related to the drying rate, is increased. However, the length of the interval during which there is a measurable contribution to F decreases with increasing k. This duration effect is stronger and hence we see that the overall accumulated flux decreases with k. Therefore, the solutions presented replicate well the salient features of trapping skinning.

NOMENCLATURE

The equation number where a particular quantity first appears is listed. Quantities with tildes have dimensions; other quantities are dimensionless.

Roman Letters

a	Coefficient in flux-front speed relationship (4)
$C(x, t)$	Concentration of penetrant at position x and time t (1a)
$D(C)$	Binary diffusion coefficient for system (1a)
De	Integral sorption Deborah number for system, value D_r (5)
F	Accumulated flux through the boundary (6)
k	Parameter describing the permeability of the exposed surface (3)
L	Typical length scale (5)
$s(t)$	Position of glass-rubber interface, defined as $C(s(t), t) = C_*$ (4)
t	Time from beginning of experiment (1a)
x	Distance from boundary (1a)
z	Scaled time variable, value $k^2 t/\kappa^2$ (9)

Greek Letters

β (C)	Inverse of the relaxation time (1b)
γ	Parameter in stress evolution equation (1b)
ϵ	Perturbation expansion parameter, value β_g/β_r (1b)
κ	Parameter, value $\sqrt{D_r + \gamma}$ (7)
$\sigma(x, t)$	Stress in polymer at position x and time t (1a)

Other Notation

g	As a subscript, used to indicate the glassy state (1b)
r	As a subscript, used to indicate the rubbery state (2a)
$*$	As a subscript, used to indicate a quantity at the transition value between the glassy and rubbery states (2a)
	Used to indicate differentiation with respect to t (4)
∞	As a subscript, used to indicate a term in an expansion for large t (16)

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