An asymptotic analysis of polymer desorption and skinning

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SUMMARY: During desorption of penetrant-saturated polymers, a glassy skin can form at the exposed surface. The associated dynamics are not purely Fickian due to viscoelastic relaxation effects in the polymer. A model is presented which captures these nonlocal effects. The motion of the glass-rubber interface and the accumulated desorbed flux are calculated. The model also describes trapping skinning, where an increase in the driving force reduces the amount of penetrant released.

Introduction

One unusual feature of polymer-penetrant systems is a change in the polymer from a *rubbery* state when it is nearly saturated to a *glassy* state when it is nearly dry. Sometimes a glassy skin develops at the exposed surface when a saturated polymer film or fiber is desorbed. This phenomenon is called *literal skinning* since the polymer is now in two states – the glassy skin and the deeper rubbery material[1–3]. Because the diffusion coefficient in the glassy skin is much lower than in the rubbery region, desorption of saturated films may be slowed[4]; such effects must be taken into account in various industrial processes[3, 5, 6].

When certain polymer-penetrant systems are desorbed, an even more unusual phenomenon called *trapping skinning* can occur. An increase in the driving force for the desorption will usually increase the accumulated flux through an exposed surface. Trapping skinning occurs when an increase in the force driving the desorption *decreases* the accumulated flux. This behavior cannot be fully explained by the lower molecular diffusion coefficient in the skin[2, 3, 7, 8].

Though these anomalous phenomena incorporate numerous physical mechanisms, one important factor is a viscoelastic stress in the polymer entanglement network. This stress, which is a nonlinear memory effect, depends on the polymer's relaxation time[9–11]. Edwards and Cohen[12, 13] have derived a set of model equations for general polymer-penetrant systems of this type, though most studies of this model have been concerned with sorption experiments[12–16]. There has been one study of desorption using this model[17], but the results do not extend to the case of arbitrary concentrations of the penetrant in the external environment.

Two physical quantities are of particular interest when modeling desorption processes: the motion of the glass-rubber interface and the accumulated flux through the boundary. We shall describe each of these quantities in terms of dimensionless parameters for the desorption problem with arbitrary exterior concentration.

Governing equations

Though the diffusion coefficient D in such polymer-penetrant systems may vary severely with concentration[18], Crank[7] and Crank and Park[8] note that the lower diffusion coefficient in the glassy region is not enough to explain trapping skinning. Therefore, though a Fickian-type model may capture the dynamics in the rubbery region, for diffusion in the skin a more sophisticated model must be employed.

Thus, motivated by the discussion in the Introduction, we postulate that the chemical potential depends not only on the dimensionless concentration C, but also on the stress σ in the polymer network[12]. Deriving the mass balance law from the chemical potential, we obtain the following dimensionless equations[17]:

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

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

where $\beta(C)$ is the inverse of the relaxation time and γ is a positive constant. Note that Eq. (1b) is similar to the evolution equation for viscoelastic stress, but recall that σ is the stress for the polymer network, rather than the total stress in the system.

The glassy state of the polymer (denoted by sub- and superscripts g) is defined as having $C < C_*$, where C_* is the glass-rubber transition concentration; the rubbery state (denoted by sub- and superscripts r) is defined as having $C > C_*$. In order to obtain a system which is amenable to asymptotic techniques, we approximate $\beta(C)$ and $D(C)$ by their averages in each state, thus obtaining a piecewise constant form, as in Crank[19].

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Though such choices are obviously idealizations of the true behavior, models with such forms for D and β have produced qualitative agreement with various experimental phenomena[12, 20, 21].

The piecewise-constant form for β is motivated by the fact that the relaxation time decreases radically at the glass-rubber transition, which causes a corresponding increase in β[22, 23]. Hence, we let $\beta_g/\beta_r = \varepsilon$, where $0 < \varepsilon \ll 1$, and use it as our perturbation parameter. In addition, a severe increase in D is localized about the glass-rubber interface where $C = C_*$[9, 20, 22–26], so we set $D_g = O(\varepsilon)$. This small diffusion coefficient can inhibit the desorption process if a glassy skin forms. Since D_g is so small, the dominant contribution to the flux in the glassy region is given by the stress term. This agrees with the observation that nonlinear relaxation effects are most pronounced in the glassy region.

We model the desorption of a polymer which is initially saturated, so $C(x, 0) = 1$. Since any prestressing decays away on a fast time scale[27], we treat the polymer as initially unstressed, so $\sigma(x, 0) = 0$. We choose a highly permeable exterior surface, so the radiation condition there reduces to $C(0, t) = C_{\text{ext}}$, where C_{ext} is the concentration of the penetrant in the external environment. Our problem will involve matching solutions in the glassy and rubbery states. Thus, it is necessary to impose conditions at the moving boundary $x = s(t)$ separating the two regions. Since no additional physical processes occur at the glass/rubber transition, these conditions are continuity of the penetrant concentration at the transition value C_*, continuity of stress, and continuity of flux[28].

By modeling the polymer as a semi-infinite slab, we are able to neglect shrinking of the polymer matrix as it is desorbed[3]. However, we expect the effects of such shrinkage to manifest themselves through a negative (compressive) stress. The C_t term in Eq. (1b) is negative, while γ is positive. Therefore, we may obtain a negative stress if we allow the C_t term to dominate by setting $\gamma = O(\varepsilon)$. This model then corresponds to the one proposed by Tang[29] and refined and studied by Durning and his colleagues[3, 22, 30, 31].

The two states

Using the aforementioned sizes for our parameters, in the rubbery region equations (1) become, to leading order,

$$C_t^r = \mathrm{De}\, C_{xx}^r \qquad x > s(t), \qquad t > 0 \tag{2a}$$

$$\sigma^r \equiv 0 \tag{2b}$$

where $\mathrm{De} = D_r$ is the integral sorption Deborah number for the system defined in Wu and Peppas[32]. We note from Eq. (2b) that to leading order the rubbery polymer entanglement network is stress-free. Hence viscoelastic effects are unimportant and we obtain the Fickian equation (2a).

If $C_{\text{ext}} \geq C_*$, the entire polymer is always rubbery and the purely Fickian solution may be obtained using standard techniques. However, if $C_{\text{ext}} < C_*$, the polymer must immediately develop a glassy skin at the boundary. Since there are now two states in the polymer, we must solve the full moving boundary-value problem. Using Eq. (2b) and information from the next-order stress term in the rubbery region, continuity of flux at the glass-rubber interface may be written as

$$C_x^g(s(t), t) = \mathrm{De}\, C_x^r(s(t), t) \tag{3}$$

The left-hand side of Eq. (3) actually arises from the stress term, which dominates the flux since $D_g = O(\varepsilon)$. However, molecular diffusion dominates in the rubbery region, as indicated by the form of Eq. (2a).

Using the aforementioned sizes for our parameters, in the glassy region equations (1) become, to leading order,

$$C_{tt}^g + C_t^g = C_{xxt}^g \qquad 0 < x < s(t), \qquad t > 0 \tag{4a}$$

$$\sigma_t^g + \sigma^g = C_t^g \tag{4b}$$

Note that the left-hand sides of our operators indicate an underlying e^{-t} behavior, not only in the stress, but also in the concentration. This is a direct result of viscoelastic memory effects.

Asymptotics

One can write the solution to the system of equations (2)–(4) as a set of integral equations. Performing small-time asymptotics on these integral equations subject to the front conditions, we have the following short-time expression for the glass-rubber interface[27]:

$$\begin{gathered} s(t) \sim 2 s_0 \sqrt{t} \\ \frac{(C_* - C_{\text{ext}})\ \exp(-s_0^2)}{\operatorname{erf} s_0} = \frac{(1 - C_*)\ \exp(-s_0^2/\mathrm{De})\sqrt{\mathrm{De}}}{\operatorname{erfc}(s_0/\sqrt{\mathrm{De}})}, \\ t \to 0 \end{gathered} \tag{5}$$

We note that the front moves in a Fickian way because the memory terms have not had time to evolve. As C_* increases, not as much penetrant needs to desorb in order for the solution to attain C_* at the front, so s_0 increases. As De increases, the flux into the front from the rubbery region poses a greater barrier to surmount in order to propagate the front, and hence s_0 decreases. As C_{ext} increases, the flux out of the front to the glassy region is smaller, and so s_0 decreases in this case as well.

Graphs of the calculated values of C vs. x for various values of t are shown in Fig. 1. Gaps appear in the graph due to the fact that we solve the front condition asympto-

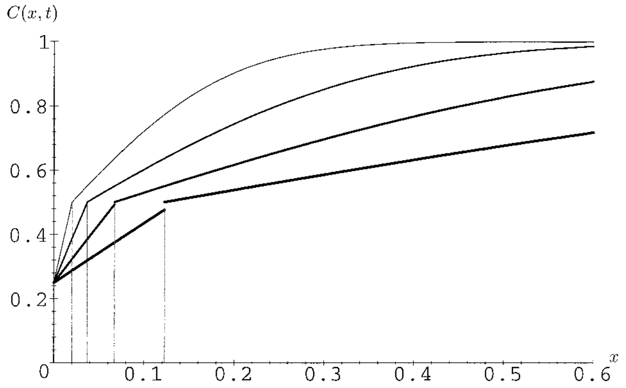

Fig. 1. $C(x,t)$ vs. x for $C_* = 1/2$, $\mathrm{De} = 4$, $C_{\text{ext}} = 1/4$. In increasing order of thickness: $t = 0.0027$, 0.009, 0.03, and 0.1. The vertical lines indicate the glass-rubber transition

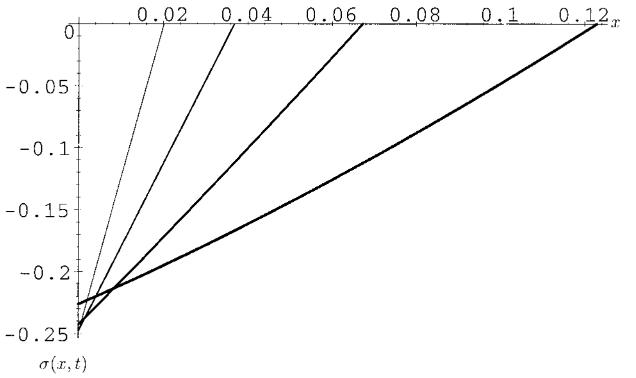

Fig. 2. $\sigma(x,t)$ vs. x for $C_* = 1/2$, $\mathrm{De} = 4$, $C_{\text{ext}} = 1/4$. In increasing order of thickness: $t = 0.0027$, 0.009, 0.03, and 0.1. The glass transition occurs where the curves intersect the σ-axis

tically rather than exactly. Though the flux is continuous across the front, C_x is *not* since the flux now has two components. The memory effects have not yet had enough time to become dominant, so the profiles are qualitatively similar to those for Fickian diffusion. Graphs of σ vs. x for various values of t are shown in Fig. 2. We note the negative (compressive) stress in the polymer entanglement network.

Performing large-time asymptotics on the integral equations subject to the front conditions, we have the following long-time expression for the glass-rubber interface[27]:

$$\begin{aligned} s(t) &\sim 2s_\infty t \\ s_\infty &= \frac{C_* - C_{\text{ext}}}{2\sqrt{(1-C_{\text{ext}})(1-C_*)}}, \qquad t \to \infty \end{aligned} \tag{6}$$

We note that for large time, we have a constant front speed which is independent of De. Thus, Fickian diffusion is now dominated by viscoelastic memory effects. As expected, the larger the differential between the exterior concentration C_{ext} and the transition concentration C_*, the faster the front will move.

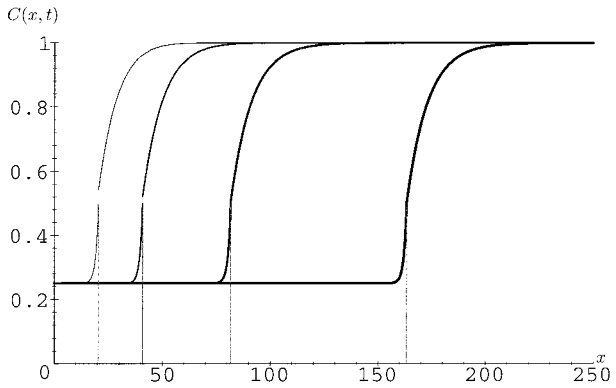

Fig. 3. $C(x,t)$ vs. x for $C_* = 1/2$, $\mathrm{De} = 4$, $C_{\text{ext}} = 1/4$. In increasing order of thickness: $t = 50$, 100, 200, 400. The vertical lines indicate the glass-rubber transition

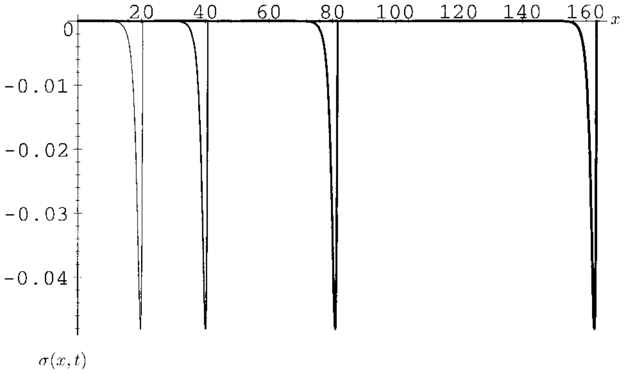

Fig. 4. $\sigma(x,t)$ vs. x for $C_* = 1/2$, $\mathrm{De} = 4$, $C_{\text{ext}} = 1/4$. In increasing order of thickness: $t = 50$, 100, 200, 400. The glass transition occurs where the curves intersect the σ-axis after the peak

Graphs of C vs. x for various values of t are shown in Fig. 3. Once again, gaps form in the graph when the asymptotics begin to lose validity. Due to the latent e^{-t} behavior in C^g, a glassy skin develops where the concentration in the polymer is within e^{-t} of that in the external environment.

Graphs of σ vs. x for various values of t are shown in Fig. 4. Once again, we have a negative (compressive) stress in the polymer network. Instead of the monotonic behavior of the stress for small time, we note that for large t, the magnitude of the stress attains a maximum value behind the glass-rubber interface. Hence the stress builds up in the glassy region before being released near the glass-rubber interface as a result of the disentangling of the polymer network. This type of behavior has been seen previously in this model in sorption studies[15].

Some remarks on trapping skinning

To investigate the existence of trapping skinning, we define F to be the accumulated flux through the exposed boundary. The driving force for the desorption can be enhanced by reducing C_{ext}, which forces a greater flux through the exposed surface.

If $C_{\text{ext}} > C_*$, the polymer is always rubbery, so we obtain the following Fickian-type result:

$$F = 2(1 - C_{\text{ext}})\sqrt{\frac{\text{De}}{\pi}} \lim_{t \to \infty} \sqrt{t} \tag{7}$$

Since the polymer is taken to be semi-infinite, an infinite amount of penetrant is desorbed. This divergence of the flux is a direct result of the Fickian nature of the leading-order operator.

If $C_{\text{ext}} < C_*$, the polymer at the exposed boundary is always glassy. Note from Fig. 3 and Fig. 4 that the flux through the exposed surface is exponentially small for large t. Though we cannot explicitly compute a closed form for F, this fact provides strong evidence that F is finite[27]. If this is indeed the case, decreasing C_{ext} (and hence increasing the driving force) has reduced the flux desorbed from an infinite to a finite quantity. Therefore, we believe that the polymer system we are modeling does exhibit trapping skinning.

Conclusions

During the desorption of saturated polymers, a glassy skin can form at the exposed surface. The formation of such a skin slows desorption[4] because the molecular diffusion coefficient is smaller in the glassy region[1–3]. In addition, trapping skinning can occur, so an increase in the driving force will decrease the total flux through the exposed surface. Molecular diffusion alone cannot describe such behavior; rather, viscoelastic memory effects must also be considered[2, 3, 7, 8].

Due to the highly permeable interface, C_{ext} determines the state of the polymer at the exposed surface. If $C_{\text{ext}} \geq C_*$, the polymer is always rubbery, and the resulting problem can be solved in closed form. Since memory effects are negligible in the rubbery state[23], the solution behaves in a purely Fickian way, and due to the infinite extent of the polymer, the accumulated flux through the exposed surface diverges like $t^{1/2}$.

When $C_{\text{ext}} \leq C_*$, there is an instantaneous change in the polymer from rubber to glass at the exposed surface. The glass-rubber interface initially moves like $t^{1/2}$ since the memory has not had time to develop. As time progresses, the front moves with constant speed, as in case II diffusion in sorption experiments[33]. Since the underlying nature of the operator in the glassy region (Eq. (4a)) has an exponential decay in time, there is strong evidence that the accumulated flux is finite for this case. Since decreasing C_{ext} corresponds to increasing the driving force, this phenomenon corresponds to trapping skinning.

Nomenclature

The equation number where a particular quantity first appears is listed, if applicable.

$C(x, t)$	concentration of penetrant at position x and time t (Eq. (1a))
$D(C)$	molecular diffusion coefficient for system (Eq. (1a))
De	integral sorption Deborah number for the system (Eq. (2a))
F	accumulated flux through the exposed surface
$s(t)$	position of glass-rubber interface, defined by $C(s(t), t) = C_*$
t	time from beginning of experiment (Eq. (1a))
x	distance from boundary (Eq. (1a))
$\beta(C)$	inverse of the relaxation time (Eq. (1b))
γ	dimensionless parameter (Eq. (1b))
ε	perturbation expansion parameter, value β_g/β_r
$\sigma(x, t)$	stress in polymer entanglement network at position x and time t (Eq. (1a))

Other notation

ext	as a subscript, used to indicate a value exterior to the polymer
g	as a sub- or superscript, used to indicate the glassy state (Eq. (1b))
r	as a sub- or superscript, used to indicate the rubbery state
0	as a subscript, used to indicate a term in an expansion for small t (Eq. (5))
$*$	as a subscript, used to indicate a quantity at the transition value between the glassy and rubbery states
∞	as a subscript, used to indicate a term in an expansion for large t (Eq. (6))

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