Surface Concentration Effects in the Drying of Solvent-Coated Polymer Films

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SYNOPSIS

The effect of changing the solvent surface concentration on the initial rate of solvent removal from solvent-coated polymer films is investigated. An analytical perturbation solution is developed for the nonlinear problem, and predictions are made for different surface concentrations and different diffusivity–concentration dependencies. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

An important step in the manufacture of polymer films and synthetic fibers is the drying of polymer solutions.[1] In the usual case of the drying of a binary solution, an increase in the vapor pressure of the solvent in the gas phase will lead to a decrease in the rate of removal of the solvent from the liquid film. However, Crank[2] has noted that instances have been reported where an increase in the solvent vapor pressure at the surface of the liquid film produces an increased rate of drying. Crank cites an example from a British patent where it appears that the rate of solvent loss from polymer filaments was increased by using an increased amount of solvent vapor in the gas phase. This apparently anomalous behavior was attributed to the concentration dependence of the diffusion coefficient, namely that the diffusion coefficient is very small for a nearly dry polymer. The part of the film near the surface acts as a barrier to solvent evaporation when there is no solvent in the gas phase since the solvent surface concentration in the liquid is zero and the diffusion coefficient is very low. When there is solvent vapor in the gas phase, there can be a significant concentration of solvent at the liquid surface and the diffusion coefficient can be significantly higher. It could thus be argued that the presence of a larger

diffusivity near the surface could lead to a faster drying rate.

Crank[2] has presented solutions for the unsteady drying of a polymer film, which he claims show that the anomalous drying process described above cannot be explained by the concentration dependence of the diffusion coefficient. He concludes that his unsteady drying-process calculations do not support the view that the rate of solvent loss from a polymer film can be increased by increasing the concentration of solvent at the liquid surface. Crank further concludes that such anomalous effects in the drying of polymer films must be caused by factors other than a Fickian diffusion process with a concentration-dependent diffusivity.

Crank[2] effectively investigated only a single diffusivity–concentration relationship, and it seems useful to see what effect different diffusivity–concentration dependencies and different surface concentrations have on the *initial* rate of solvent removal from polymer films. The problem is formulated in the second section of this paper, and a perturbation solution to the nonlinear problem is developed in the third section. The results of the analysis are presented and discussed in the fourth section of the paper. The basic objective in this study is to determine what effects the strength of the concentration dependence of the diffusivity and the solvent surface concentration have on the drying rate. (The initial rate of solvent removal is used here.) The present study thus represents a more comprehensive investigation of surface concentration effects in the drying of solvent-coated polymer films.

PROBLEM FORMULATION

Consider the unsteady, one-dimensional, isothermal drying of a polymer film of thickness L. The film is a binary solution of a nonvolatile polymer and a volatile solvent, and there are no chemical reactions in the liquid phase. The polymer film extends from an impermeable solid boundary at $x = 0$ to the gas–liquid interface at $x = L$, and the concentration of solvent in the film is small enough that there is a negligible movement of the gas–liquid interface. There is also a negligible external mass transfer resistance so that the gas phase concentration of the solvent is in equilibrium with the liquid solvent concentration at the gas–liquid surface. Finally, the mutual diffusion coefficient is generally a function of the solvent concentration, but the partial specific volumes of the polymer and solvent are independent of concentration.

The above unsteady Fickian diffusion problem is described by the following dimensionless set of equations:

$$\frac{\partial \phi}{\partial \tau} = \frac{\partial}{\partial \xi}\left(\frac{D}{D_0}\frac{\partial \phi}{\partial \xi}\right) \tag{1}$$

$$\frac{\partial \phi}{\partial \xi} = 0, \quad \xi = 0 \tag{2}$$

$$\phi = 1, \quad \xi = 1 \tag{3}$$

$$\phi = 0, \quad \tau = 0 \tag{4}$$

$$\phi = \frac{C - C_0}{C_g - C_0} \tag{5}$$

$$\xi = \frac{x}{L} \tag{6}$$

$$\tau = \frac{D_0 t}{L^2} \tag{7}$$

In these equations, x is the space variable in the diffusion direction, t is time, C is the solvent mass density, C_0 is the initial solvent mass density, and C_g is the solvent mass density at the liquid surface which is in equilibrium with the solvent concentration in the gas phase. Also, D is the concentration-dependent binary mutual diffusion coefficient, and D_0 is the mutual diffusion coefficient at $C = 0$.

Integration of eq. (1) from $\xi = 0$ to $\xi = 1$ and introduction of eq. (2) produces the following expression:

$$\frac{d}{d\tau}\left[\int_0^1 \phi \, d\xi\right] = \frac{D_s}{D_0}\left(\frac{\partial \phi}{\partial \xi}\right)_{\xi=1} \tag{8}$$

where D_s is the diffusivity at the gas–liquid interface:

$$D_s = D(\xi = 1) \tag{9}$$

In addition, it can be shown that

$$\int_0^1 \phi \, d\xi = \frac{M}{M_\infty} \tag{10}$$

where M is the mass of solvent per unit area that has left the film at time τ, and M_∞ is the mass of solvent per unit area that has left the film at time $\tau = \infty$. Hence, the combination of eqs. (8) and (10) yields the following result for the time dependence of M/M_∞:

$$\frac{d}{d\tau}\left[\frac{M}{M_\infty}\right] = \frac{D_s}{D_0}\left(\frac{\partial \phi}{\partial \xi}\right)_{\xi=1} \tag{11}$$

In the initial stages of the mass transfer process, the liquid film is effectively a semi-infinite medium, so it is convenient to introduce the coordinate transformation

$$z = 1 - \xi \tag{12}$$

and suppose that the liquid film goes from $z = 0$ to $z = \infty$. Hence, eqs. (1) through (4) are replaced by the following set of equations:

$$\frac{\partial \phi}{\partial \tau} = \frac{\partial}{\partial z}\left(\frac{D}{D_0}\frac{\partial \phi}{\partial z}\right) \tag{13}$$

$$\phi = 1, \quad z = 0 \tag{14}$$

$$\phi = 0, \quad z = \infty \tag{15}$$

$$\phi = 0, \quad \tau = 0 \tag{16}$$

In addition, introduction of the variable

$$y = \frac{z}{2\tau^{1/2}} \tag{17}$$

reduces the above problem to the following simpler form:

$$\frac{d}{dy}\left[\frac{D}{D_0}\frac{d\phi}{dy}\right] + 2y\frac{d\phi}{dy} = 0 \qquad (18)$$

$$\phi = 1, y = 0 \qquad (19)$$

$$\phi = 0, y = \infty \qquad (20)$$

Furthermore, substitution of the y variable in eq. (11) and integration yield the following expression for the time dependence of M/M_∞:

$$\frac{M}{M_\infty} = -\frac{D_s}{D_0}\left(\frac{d\phi}{dy}\right)_{y=0}\tau^{1/2} \qquad (21)$$

For the present investigation, we assume that the concentration dependence of the mutual diffusion coefficient D can be described by a linear relationship from $C = 0$ to $C = C_0$:

$$\frac{D}{D_0} = \left[1 + A\frac{C}{C_0}\right] \qquad (22)$$

The parameter A characterizes the strength of the concentration dependence of D, and, hence, different diffusivity–concentration dependencies can be achieved simply by adjusting A. Equation (22) can be written in the following form in terms of the dimensionless concentration ϕ:

$$\frac{D}{D_0} = 1 + A[1 + \phi(\alpha - 1)] \qquad (23)$$

where

$$\alpha = \frac{C_g}{C_0} \qquad (24)$$

In addition, since

$$\frac{D_s}{D_0} = 1 + A\alpha \qquad (25)$$

it is convenient to derive the following expression by combining eqs. (23) and (25):

$$\frac{D}{D_0} = \frac{D_s}{D_0} + A(1 - \alpha)(1 - \phi) \qquad (26)$$

Consequently, eq. (18) can be expressed as follows:

$$\left[\frac{D_s}{D_0} + A^*(1 - \phi)\right]\frac{d^2\phi}{dy^2} - A^*\left(\frac{d\phi}{dy}\right)^2 + 2y\frac{d\phi}{dy} = 0 \quad (27)$$

where

$$A^* = A(1 - \alpha) \qquad (28)$$

Equation (27) is a nonlinear ordinary differential equation which can be solved, subject to eqs. (19) and (20), to produce the concentration distributions in the film for different diffusivity–concentration relationships (different values of A) and different surface concentrations (different values of α). A solution of this equation is formulated in the next section by constructing a regular perturbation series around the constant diffusivity limit ($A = 0$, $A^* = 0$).

PERTURBATION SOLUTION

Since eq. (27) is linear when $A^* = 0$, it is convenient to formulate a regular perturbation series solution to eqs. (19), (20), and (27) of the following form:

$$\phi = \phi_0 + A^*\phi_1 + \cdots \qquad (29)$$

Substitution of eq. (29) into eqs. (19), (20), and (27) produces the following equations for the zero-order and first-order terms of the perturbation series:

$$\frac{D_s}{D_0}\frac{d^2\phi_0}{dy^2} + 2y\frac{d\phi_0}{dy} = 0 \qquad (30)$$

$$\phi_0(0) = 1 \qquad (31)$$

$$\phi_0(\infty) = 0 \qquad (32)$$

$$\frac{D_s}{D_0}\frac{d^2\phi_1}{dy^2} + 2y\frac{d\phi_1}{dy} + (1 - \phi_0)\frac{d^2\phi_0}{dy^2}$$
$$-\left(\frac{d\phi_0}{dy}\right)^2 = 0 \quad (33)$$

$$\phi_1(0) = 0 \qquad (34)$$

$$\phi_1(\infty) = 0 \qquad (35)$$

The solution to eqs. (30)–(32) is simply

$$\phi_0 = erfc(yh) \qquad (36)$$

where

$$h = \left(\frac{D_0}{D_s}\right)^{1/2} \qquad (37)$$

Consequently, eq. (33) can be rewritten in the following form:

$$\frac{D_s}{D_0}\frac{d^2\phi_1}{dy^2} + 2y\frac{d\phi_1}{dy} + [1 - erfc(hy)]\left[\frac{4yh^3}{\pi^{1/2}}e^{-y^2h^2}\right]$$
$$-\frac{4h^2}{\pi}e^{-2y^2h^2} = 0 \quad (38)$$

and it can be shown that the solution to eqs. (34), (35), and (38) is given by the following expression:

$$\phi_1 = \left[-\frac{2h^{3/2}}{\pi^{1/2}}\left(\frac{1}{2} - \frac{1}{\pi}\right)\right]\frac{\pi^{1/2}}{2h}erf(hy)$$
$$+\frac{yh^3}{\pi^{1/2}}erf(yh)e^{-y^2h^2} + \frac{h^2}{2}[erf(hy)]^2$$
$$-\frac{h^2}{\pi}(1 - e^{-2h^2y^2}) \quad (39)$$

It is now possible to derive an explicit expression for M/M_∞ by using eqs. (29), (36), and (39) to evaluate the concentration derivative in eq. (21):

$$\frac{M}{M_\infty} = \frac{2}{\pi^{1/2}h}\left[1 + A^*h^2\left(\frac{1}{2} - \frac{1}{\pi}\right)\right]\tau^{1/2} \quad (40)$$

For the special case when $\alpha = 0$,

$$D_s = D_0 \quad (41)$$

$$A^* = A \quad (42)$$

and eq. (40) takes the following form:

$$\frac{M}{M_\infty} = \frac{2}{\pi^{1/2}}\left[1 + A\left(\frac{1}{2} - \frac{1}{\pi}\right)\right]\tau^{1/2} \quad (43)$$

Since it is obvious that

$$M_\infty = C_0L(\alpha - 1) \quad (44)$$

it is possible to write eq. (40) in the following form:

$$\frac{M}{C_0L} = \frac{2(\alpha - 1)}{h\pi^{1/2}}$$
$$\times \left[1 + A(1 - \alpha)h^2\left(\frac{1}{2} - \frac{1}{\pi}\right)\right]\tau^{1/2} \quad (45)$$

A reference value of M, which we denote as M_0, can be defined as follows:

$$M_0 = M(A = 0, \alpha = 0) \quad (46)$$

Clearly, M_0 is the mass of solvent per unit area that has left the film at time τ when the surface concentration is zero and when the diffusion coefficient is constant. From eqs. (25), (45), and (46), it is possible to derive the following expression:

$$\frac{M}{M_0} = (1 - \alpha)[1 + A\alpha]^{1/2}[1 + \bar{A}] \quad (47)$$

$$\bar{A} = \frac{A(1 - \alpha)\left(\frac{1}{2} - \frac{1}{\pi}\right)}{1 + A\alpha} \quad (48)$$

Equation (47) can be used to determine how M changes as the concentration dependence of D is increased (A is increased from $A = 0$) and as the surface concentration of solvent is increased (α is increased from $\alpha = 0$).

The bracketed term in eq. (43) and the quantity $[1 + \bar{A}]$ in eq. (47) represent two-term perturbation estimates of the exact result for the concentration derivative. It is, of course, possible to derive higher order approximations for the concentration derivative, but the labor involved rapidly becomes excessive. However, a closed form estimate of the perturbation series can be formulated by considering the solution presented by Wilkins[3] for the case when the mutual diffusion coefficient is proportional to the concentration of solvent. This solution suggests that, at high values of A, M/M_∞ should be proportional to the square root of A. Hence, closed-form estimates of eqs. (43) and (47) can be written as follows:

$$\frac{M}{M_\infty} = \frac{2}{\pi^{1/2}}\left[1 + 2A\left(\frac{1}{2} - \frac{1}{\pi}\right)\right]^{1/2}\tau^{1/2} \quad (49)$$

$$\frac{M}{M_0} = (1 - \alpha)[1 + A\alpha]^{1/2}[1 + 2\bar{A}]^{1/2} \quad (50)$$

Equations (49) and (50) clearly reduce to eqs. (43) and (47), respectively, for low values of A (and, hence, $\bar{A}$). Equation (49) is used below to compare the predictions of the perturbation series for the special case of $\alpha = 0$ for the initial stages of the mass transfer process with the exact numerical results of Crank.[4] This comparison will establish the range of A over which the perturbation series gives acceptable predictions for M/M_∞ and, hence, for M/M_0. Equations (48) and (50) are used in the next section to

determine the effect of A and α on M/M_0 for the initial stages of the mass transfer process.

RESULTS AND DISCUSSION

The predictions of eq. (49) for the special case of α = 0 are compared with the exact numerical results of Crank[4] in Figure 1. This figure illustrates the variation of the quantity Q with A

$$Q = \frac{M}{M_\infty \tau^{1/2}} \qquad (51)$$

over a wide range of A (1–1,000) in the initial stages of the mass transfer process for the special case when the solvent surface concentration is zero (α = 0). There is very good agreement between the analytical perturbation solution given by eq. (49) and the exact numerical results of Crank (solid circles in Fig. 1) over the range where numerical results are available ($A \leq 25$). For higher values of A, there is good agreement between the predictions of the perturbation solution and the limiting special solution of Wilkins[3] (solid squares in Fig. 1). For the range of A considered in Figure 1, the maximum error is about 3%; thus it is fair to conclude that the ana-

lytical perturbation solution should provide predictions comparable to exact numerical results for all values of A.

The dependence of M/M_0 on α for various values of A can be computed using eqs. (48) and (50). The quantity M/M_0 is of course simply the ratio of the amount of solvent that has left the film at time τ to the amount of solvent loss at τ for the reference case with α = 0 and A = 0 (zero solvent surface concentration and constant diffusivity). The above calculation is, of course, valid for the initial stages of the mass transfer process. It is convenient to define a quantity W as follows:

$$W = \frac{\dfrac{M}{M_0}(A, \alpha)}{\dfrac{M}{M_0}(A, 0)} \qquad (52)$$

The quantity W is simply the ratio of the amount of solvent that has left the film at time τ when the surface concentration is characterized by the parameter $0 < \alpha < 1$ to the loss at τ when the surface concentration is zero. The dependence of W on α for fixed A clearly illustrates what effect the solvent surface concentration has on the initial stages of the
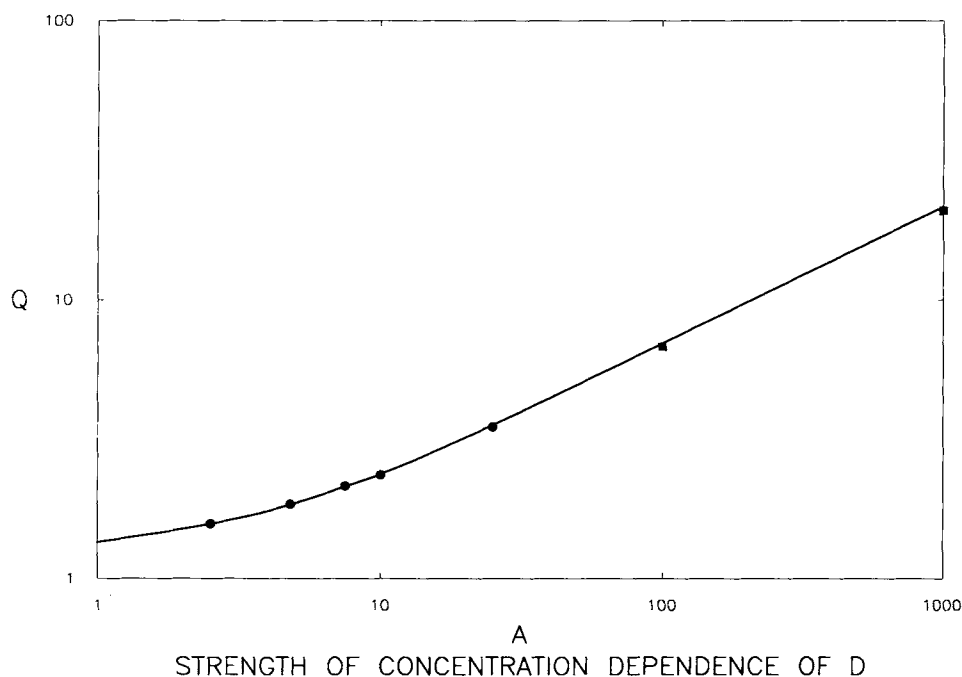

STRENGTH OF CONCENTRATION DEPENDENCE OF D

Figure 1   Comparison of Q versus A dependence for analytical perturbation solution (curve), for numerical results of Crank[4] (solid circles), and for limiting special solution of Wilkins[3] (solid squares).

drying process for a particular system of interest. The variation of W with α for three values of A is illustrated in Figure 2. From the results of this figure, it is possible to state the following two conclusions:

1. The quantity W (and hence the amount of solvent removed in the initial stages of the drying process) decreases as the surface concentration (α) increases. In addition, the W-versus-α curve approaches an asymptotic limit as A increases. This is evident from Figure 2, which shows little difference between the predictions for $A = 10$ and $A = 1,000$. Consequently, the above theoretical results show that W does not exceed unity even when the polymer–solvent system exhibits a very strong diffusivity-concentration dependence. These results agree with Crank's conclusion[2] that the solvent loss from a polymer film cannot be increased by increasing the concentration of solvent at the liquid surface. Crank arrived at this conclusion by using calculations based on a single diffusivity-concentration relationship and on general reasoning for a hypothetical diffusion coefficient which is zero at low solvent concentrations. Here, the diffusivity-concentration relationship can be varied systematically by changing the parameter A, and quantitative results can be obtained at each value of A. In addition, the perturbation solution shows quantitatively that W must still decrease monotonically with α even when A is very large. This important

result appears to exclude the possibility that W can achieve values greater than unity if A is large enough.

2. Although the perturbation solution shows that W decreases with increasing α even for large values of A, it is evident from Figure 2 that the rate of decrease is significantly less for high values of A (a stronger diffusivity-concentration relationship) for low values of α. Hence, for $A = 1,000$, there is little difference in the amount of solvent removed between $\alpha = 0$ and $\alpha = 0.1$. This important result makes it possible to have a significant solvent concentration at the liquid surface with little loss in drying efficiency. Hence, it may be possible in the initial stages of the drying process to prevent the formation of a skin at the surface of the film by keeping some solvent vapor in the gas phase. The presence of solvent at the liquid surface can help prevent solidification of the coating surface, and this can be done in certain cases without affecting the mass transfer process significantly.

It is evident from the above discussion that the solvent loss at a given time in the initial stages of the drying process cannot be increased by increasing the solvent surface concentration even if the diffusivity is a very strong function of concentration. However, as noted above, W decreases more slowly with increasing α if A is sufficiently large. It is thus feasible to keep solvent in the vapor phase to prevent solidification of the coating sur-
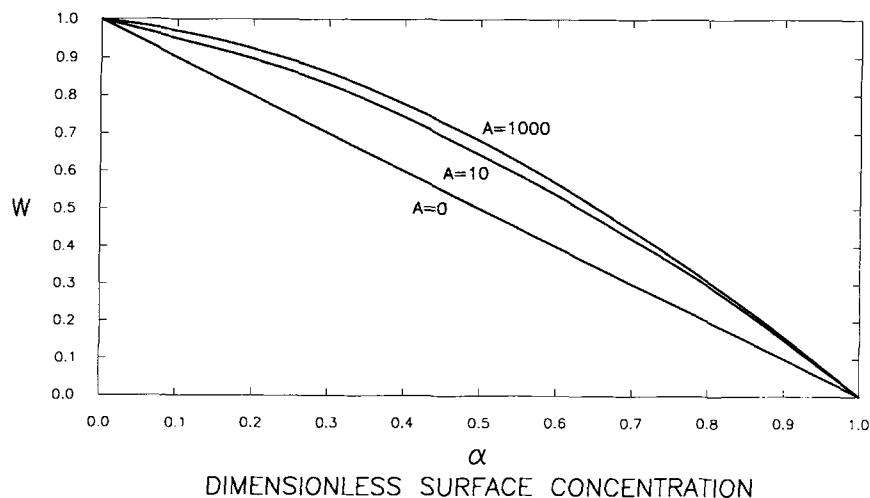

Figure 2   Dependence of W on A and α.

face; this in itself may, in some way not directly related to simple Fickian diffusion, prove beneficial in the drying process. Although the above development and conclusions are, strictly speaking, valid only for a linear diffusivity-concentration relationship, it is reasonable to expect that similar results will be obtained for other realistic D-versus-C relationships.

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