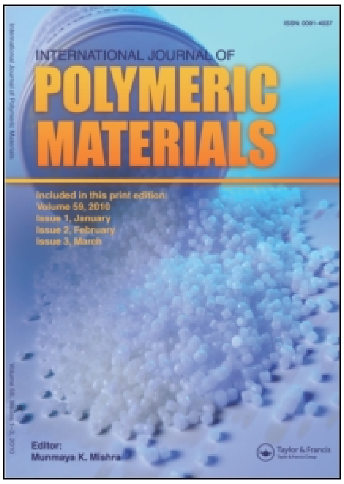

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Diffusion in Polymers with Concentration Dependent Diffusivity

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Diffusion coefficients of several solute-polymer systems can be characterized by an exponentially dependent function $D = D_o \mathrm{Exp}(AC)$. The cumulative mass uptake after a step increase of the solute concentration at the surface was considered using a film with a finite thickness and a semi-infinite domain. For finite film the diffusion equation was solved numerically by the Crank–Nicholson method. The results showed that at the beginning stage the mass uptake is proportional to $\sqrt{t}$ for both constant diffusivity and concentration dependent diffusivity. For a semi-infinite domain a transformation of variables led to a nonlinear second order ordinary differential equation which can be solved numerically to obtain the concentration function. The results of mass uptake using the Crank–Nicholson calculation on a finite thickness agree with the results of a semi-infinite calculation in the short time region. It is concluded that the diffusion coefficient as a function of concentration can be determined experimentally from the results of short-term absorption using a series of solute concentrations.

Keywords: Diffusion in polymers; Crank–Nicholson method

INTRODUCTION

Small molecules dispersed in a polymeric matrix often play important roles in the determination of the mechanical properties of the polymer. For hydrophilic polymers, such as polyamides, among many effects, the presence of water molecules may change the glass

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*Corresponding author. e-mail: Jan_Huang@uml.edu transition temperature, break down the molecular chains, and affect the barrier and mechanical properties significantly [1 – 3]. Several mechanical properties of nylon-6,6 [4] and glass filled nylon-6,6 [5] were studied in previous studies. It has been reported that moisture in nylon reduced the permeation of other small molecules through polyamide films. Small molecules investigated for this effect include inorganic gases [6] and organic vapors [7 – 9].

Another important family of small molecules is plasticizers, often used in poly(vinyl chloride). Additives, such as phthalates, adipates, sebacates and phosphates, can effectively lower the glass transition temperature and heat deflection temperature, and thus significantly improve flexibility, elongation, impact strength, multiple cyclic stress life at high deformation, electrical conduction and processability. However, being small molecules, plasticizers may migrate from the polymeric matrix over a long period of time, especially at elevated temperature [10 – 12], resulting in the deterioration of the previously mentioned mechanical properties.

At low solute concentration, diffusivity is a constant which depends on the size of solute molecules and the mobility of polymer molecules. When the concentration of the solute increases the diffusivity generally increases. It can be explained by the increase of free volume and mobility of polymer molecules. Early work was summarized by Crank and Park [13]. Recent discussions on diffusion in polymers are available in several books [14 – 16]. When the diffusivity function is plotted *vs.* concentration of solute on a semi-log scale a straight line can usually be observed. The diffusivity can be expressed as $D = D_o \operatorname{Exp}(AC)$ over a sufficient concentration range.

Diffusivity of low molecular weight solutes is usually measured by weight increase of samples. A sorption curve, mass uptake *vs.* $\sqrt{t}$, is measured in order to obtain the diffusion coefficient and it may take up to 100 days for a thick sample to reach equilibrium [4, 5, 17]. However, it is hard to keep temperature and solute concentration constant during this extremely long period of time, and the use of the whole curve to obtain information about the concentration dependence of diffusivity will incur some error. One possibility is to study the concentration dependence from a series of short term measurements using different solute concentrations. In this study, the mass uptake in short time adsorption is studied for constant diffusivity and concentration dependent diffusivity, and the possibility of reconstructing the diffusivity function is discussed.

CRANK-NICHOLSON METHOD

The diffusion of small molecules into a polymeric matrix can be described by a diffusion equation. When the diffusion coefficient D is a function of concentration the equation for one-dimensional diffusion is:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial t}\left(D\frac{\partial C}{\partial t}\right) \tag{1}$$

In the study of diffusion of small molecules in polymer films the polymer is initially free of the small molecules. The film is brought into contact with a certain concentration of the diffusant. The increase of polymer weight is measured as a function of time. The analytical solution for the normalized mass uptake *versus* time has been solved for the case of constant diffusivity [18]. The expression for short time is:

$$M/M_o = 2\left(\frac{Dt}{L^2}\right)^{0.5}\left[1/\sqrt{\pi} + 2\sum_{n=0}^{\infty}(-1)^n \mathrm{ierfc}\left(\frac{nL}{\sqrt{Dt}}\right)\right] \tag{2}$$

where L is half of the thickness of the film. The equation predicts a linear relationship between weight increase and $\sqrt{t}/L$ at the beginning of measurement. This is Fickian type behavior. From the slope the diffusivity can be calculated. Equation (2) is a solution of a linear differential equation and does not depend on concentration of the solute.

When the diffusivity is a function of the concentration the differential equation is nonlinear. Many approaches have been developed to solve this diffusion equation. Among them, Crank-Nicholson method has been widely used and is adapted in this study [18, 19]. In the Crank-Nicholson method the film thickness is divided into equal intervals. The time of diffusion measurement is also divided into intervals. The differential equation is then converted into a finite difference equation. After rearrangement of the equation the concentration of a point at a particular time can be related to five other data points. These five data points include two nearby points at the same time, two nearby points of the previous time, and the same point of the previous time. The system of linear simultaneous equations can be solved by an iteration method or a matrix inverse Doolittle UL method [20]. In our calculation the film thickness interval, $\Delta x/L$, is chosen to be 0.02 and the time interval, $D_o\Delta t/L^2$, is 0.001. The diffusion coefficient is an exponential function $D = D_o \,\mathrm{Exp}(AC)$ and three values are used for AC_o: 0, 0.5 and 1.0.

Figure 1 shows the numerical results of M/M_∞ *vs.* D_ot/L^2 for $AC_o = 0$, 0.5 and 1.0 on a double log plot. All three lines show a straight line with a slope of 0.5 when t is lower than 0.5. The mass uptake of solute with concentration dependent diffusivity is also Fickian type at short time. Three lines are similar to each other but separated horizontally by a constant, which indicates that a different slope is obtained when mass uptake is plotted *vs.* $\sqrt{t}$ in arithmetic scale. The initial slope for M/M_∞ *versus* $\sqrt{D_ot}/L^2$ is 1.128, 1.327 and 1.573 for $AC_o = 0$, 0.5 and 1.0, respectively. The value for $AC_o = 0$ corresponds to the analytical result in Eq. (2) which is $2/\sqrt{\pi}$. The agreement is within 0.1% error in Crank–Nicholson calculation. This result indicates that when a solute with concentration dependent diffusivity is studied using only one concentration it is possible to fit

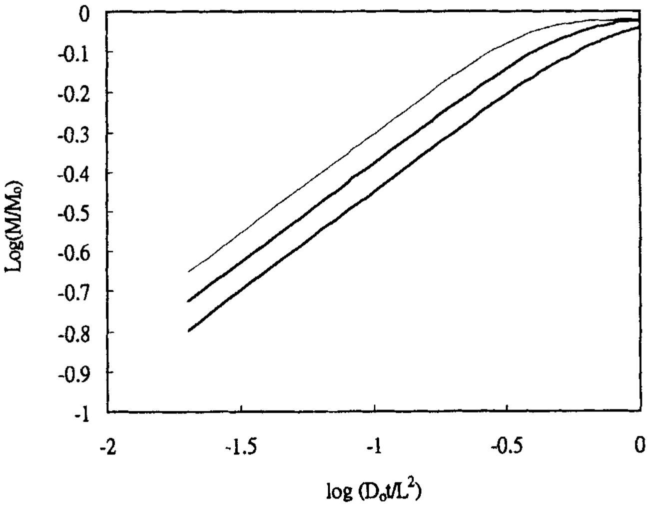

FIGURE 1 Mass uptake *vs.* D_ot/L^2 for several diffusivity functions. From left to right $AC_o = 0$, 0.5, 1.0, respectively.

the mass uptake into a linear model without displaying much error. However, when a different concentration is used a different diffusivity will be obtained.

SEMI-INFINITE DOMAIN

The boundary conditions for a semi-infinite domain subject to a step increase of concentration are:

$$C = 0 \quad t = 0 \tag{3}$$

$$C = C_o \quad x = 0 \tag{4}$$

$$C = C_o \quad x \rightarrow \infty \tag{5}$$

In the case of a semi-infinite domain, provided D is a function of C only, C may be expressed in terms of a single variable η which is defined as:

$$\eta = \frac{x}{2\sqrt{t}} \tag{6}$$

The diffusion equation can be converted to:

$$-2\eta\frac{dC}{d\eta} = \frac{d}{d\eta}\left(D\frac{dC}{d\eta}\right) \tag{7}$$

The initial and boundary conditions can be combined to:

$$C = C_o \quad \eta = 0 \tag{8}$$

$$C = 0 \quad \eta = \infty \tag{9}$$

Without an explicit expression of $D(C)$ the above equation and boundary conditions can only be solved as an implicit solution [18].

When $D = D_o \operatorname{Exp}(AC)$ a transformation can be made:

$$D = D_o \operatorname{Exp}(AC_o)u \tag{10}$$

$$u = \operatorname{Exp}[A(C - C_o)] \tag{11}$$

$$\xi = \frac{x}{\sqrt[2]{D_o t}} \operatorname{Exp}(-AC_o/2) \tag{12}$$

The following equation is obtained:

$$u\frac{d^2u}{d\xi^2} = -2\xi\frac{du}{d\xi} \tag{13}$$

The initial and boundary conditions are:

$$u = 1 \quad \xi = 0 \tag{14}$$

$$\frac{du}{d\xi} = -u'(0) \quad \xi = 0 \tag{15}$$

$$u = \mathrm{Exp}(-AC_o) \quad \xi = \infty \tag{16}$$

The above equation is a nonlinear second order differential equation. It can be solved numerically by the Runge–Kutta–Nystron method [20] with an initial condition of $u'(0)$. When ξ increases the value of u gradually decreases to a constant which is identified as $\mathrm{Exp}(-AC_o)$. The results of u *vs.* ξ are shown in Figure 2 for $u'(0) = -0.5$ and -1.0. From u the concentration can be expressed as a function of ξ or η. Note that for the constant diffusion coefficient situation $u'(0) = 0$ and $u = 1$ for all ξ. A one to one correspondence between $u'(0)$ and AC_o exists through the solution and this relation is shown in Figure 3.

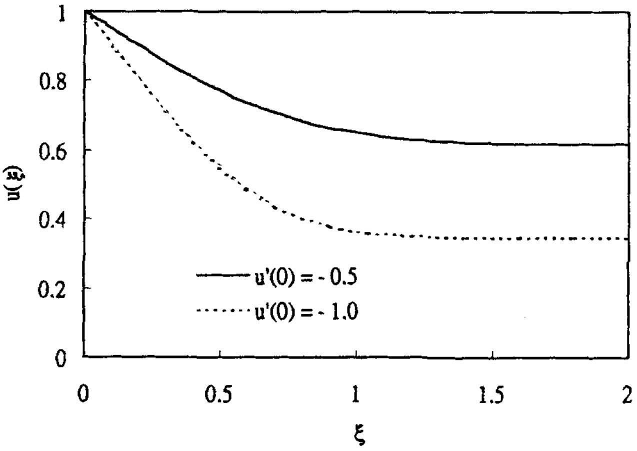

FIGURE 2 Solution of Eq. (13) with $u'(0) = -0.5$ and -1.0.

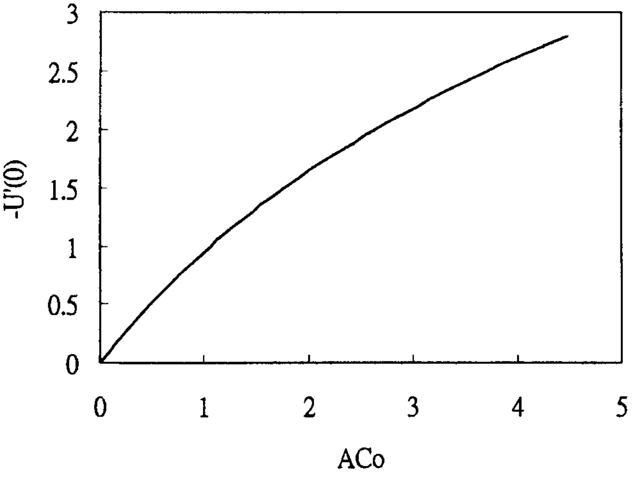

FIGURE 3 Relationship between $u'(0)$ and AC_o.

The flux into the film is calculated as:

$$J = D\frac{\partial C}{\partial x}\bigg|_{x=0} = D\frac{\partial C}{\partial \xi}\left(\frac{\partial \xi}{\partial x}\right)\bigg|_{\xi=0} = \frac{D_o \operatorname{Exp}(AC_o)}{A}\frac{du}{d\xi}\left(\frac{\partial \xi}{\partial x}\right)\bigg|_{\xi=0}$$
$$= \frac{u'(0)}{2A}\operatorname{Exp}(AC_o/2)(D_o/t)^{0.5} \tag{17}$$

The result is similar to Fickian type diffusion because it is proportional to $1/\sqrt{t}$, but the slope is a function of C_o. The cumulative amount of diffusant into the film during time t is:

$$\int_0^t J dt = \frac{\sqrt{D_o}}{AC_o} u'(0) \operatorname{Exp}(AC_o/2) C_o \sqrt{t} \tag{18}$$

By plotting the amount of mass increase per unit area *versus* $C_o\sqrt{t}$ a linear line can be obtained with a slope equal to:

$$\text{Slope} = \sqrt{D_o}\, g(AC_o) \tag{19}$$

$$\text{with} \quad g(AC_o) = \operatorname{Exp}(AC_o/2)\, u'(0)/AC_o \tag{20}$$

This slope is determined by a function $g(AC_o)$ and a constant $\sqrt{D_o}$. The function $g(AC_o)$ is a universal function of AC_o and is plotted in Figure 4. It starts at a constant value when AC_o is near zero and gradually increases when AC_o increases. When AC_o is zero a constant diffusivity exists and the value of $g(AC_o)$ reaches a value of 1.128 ($= 2/\sqrt{\pi}$) which agrees with the result of Eq. (2). For $AC_o = 0.5$ and 1.0 the value of $g(AC_o)$ is 1.320 and 1.604, respectively. Compared with the Crank–Nicholson results a discrepancy is observed and reaches 2% at $AC_o = 1.0$. When AC_o is large the diffusivity changes rapidly from the surface to the inside of the film. This may create some error in the linear approximation in the Crank–Nicholson calculation.

Both A and $\sqrt{D_o}$ can be determined from experimental results by plotting slope *versus* C_o on double log paper. The results are superimposed on separate double log paper in Figure 4. The data are moved horizontally and vertically until the best match is observed between the data and the curve in Figure 4. Since, on a log scale, a multiplication by a constant is equal to a shift of coordinate, the constant A is obtained from the horizontal coordinate and the constant $\sqrt{D_o}$ is obtained from the vertical coordinate. If the data deviate

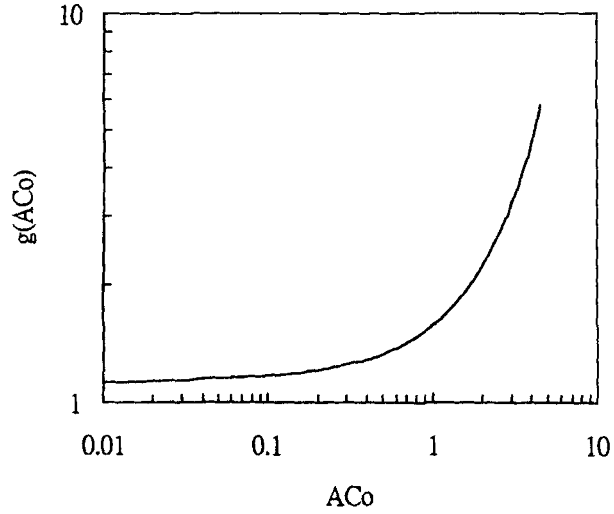

FIGURE 4 Values of function $g(AC_o)$.

from the curve shown in Figure 4 then the data are not described by $D = D_o \text{Exp}(AC)$. A different function would be required.

CONCLUSION

From the Crank–Nicholson method the mass uptake into a film is calculated for constant diffusivity and concentration dependent diffusivity. The concentration *vs.* time curves are similar on a double log scale and show a Fickian behavior at short time. The beginning slopes match the results of a semi-infinite solution. A method is provided to use the short term mass uptake to reconstruct the diffusivity function.

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