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ANOMALOUS DIFFUSION OF LIQUIDS IN GLASSY POLYMERS

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Abstract—Anomalous diffusion of liquid penetrants in glassy polymers is formulated as a moving boundary problem. The concept of volume average velocity is utilized in mathematical modelling. The model equation is solved using a method which is a combination of the method of lines and the method of invariant imbedding. The results are shown to be in agreement with the existing experimental observations.

INTRODUCTION

Solid polymers can be in two different states. Below the glass transition temperature the polymer is in a glassy state; it is a hard and brittle material. The glass transition temperature is the temperature at which a polymer changes from a glassy material to a softer, flexible rubbery material. In addition to stiffness, many other properties, such as refractive index, thermal conductivity, specific volume, dielectric constant, diffusivity, etc., differ considerably for a polymer in its two different states. The difference of these physical properties in rubbery and glassy polymer states is due to the difference of chain mobility in the two states.

All theories of diffusion in polymers, in one way or another, are based on chain mobility at the molecular level. For example, when a polymer absorbs an organic penetrant the polymer molecules rearrange toward a new equilibrium conformation. In rubbery polymers, polymer chain segments are sufficiently active to achieve this structural equilibrium instantaneously and the diffusion mechanism is Fickian and unique. However, in glassy polymers equilibrium chain conformation is not instantaneous because of the limited mobility of the polymer segments. In the latter case, different patterns of segmental motion under different conditions give rise to different diffusion mechanisms. Hence, diffusion mechanisms in glassy polymers are classified as follows [1, 2]:

1. Case I (Fickian) diffusion
2. Case II diffusion
3. Anomalous diffusion

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Table 1. Characteristics of Case I and Case II diffusion mechanisms

Case I diffusion	Case II diffusion
Penetrant mobility controls	Segmental relaxation controls
Initial weight gain proportional to $\sqrt{t}$	Initial weight gain proportional to t
Concentration variation across the swollen shell	Swollen rubbery shell in a uniform equilibrium concentration
Low activation energy	Sharp boundary* movement with a constant velocity
	High activation energy

*When liquid penetrant diffuses into a polymer, a sharp advancing boundary is observed between the inner glassy region and the outer swollen rubbery layer.

General characteristics of the two limiting types of diffusion mechanisms, Case I and Case II, are summarized in Table 1.

The diffusion mechanism in the anomalous case can be considered to be the resultant of the sum of the Case I and Case II mechanisms. For this case, experimental observations of weight gain M and boundary movement s can be expressed as a function of time in the following manner:

$$M = k_1 t^n \quad 0.5 < n < 1.0 \quad \text{or} \quad M = a_1\sqrt{t} + b_1 t \tag{1}$$

$$s = k_2 t^n \quad 0.5 < n < 1.0 \quad \text{or} \quad s = a_2\sqrt{t} + b_2 t \tag{2}$$

Although existing models [3–7] explain Case I and Case II diffusion mechanisms, they fail to predict the behavior in the so-called anomalous diffusion. The purpose of this paper is to develop a rigorous mathematical model for the anomalous diffusion mechanism and to obtain solutions to the model equation.

DERIVATION OF THE DIFFUSION EQUATION

Consider a polymer-penetrant system in which A represents the penetrant and B represents the polymer. For the penetrant, the conservation of chemical species can be written as

$$\frac{\partial \rho_A}{\partial t} + \underline{\nabla} \cdot \rho_A \underline{v}_A = r_A \tag{3}$$

where ρ_A denote the mass density of species A and r_A denote the rate of production of species A per unit volume by homogeneous chemical reaction. The mass flux of species A with respect to the volume average velocity, $\underline{v}^0$, is represented by

$$\underline{j}_A^0 = \rho_A(\underline{v}_A - \underline{v}^0) \tag{4}$$

Combining (4) with (3) and considering that $r_A = 0$ (i.e., no homogeneous reaction) yields

$$\frac{\partial \rho_A}{\partial t} + \underline{\nabla} \cdot \rho_A \underline{v}^0 = -\underline{\nabla} \cdot \underline{j}_A^0 \tag{5}$$

For a binary system, Fick's first law takes the form [8]

$$\underline{j}_A^0 = -D\underline{\nabla}\rho_A \tag{6}$$

where D is the diffusivity. Substitution of (6) into (5) gives

$$\frac{\partial \rho_A}{\partial t} + \underline{\nabla} \cdot \rho_A \underline{v}^0 = \underline{\nabla} \cdot (D\underline{\nabla}\rho_A) \tag{7}$$

Yılmaz [9] showed that the volume average velocity is either a constant or zero in many liquid diffusion processes. With this constraint (7) becomes

$$\frac{\partial \rho_A}{\partial t} + \underline{v}^0 \cdot \underline{\nabla}\rho_A = \underline{\nabla} \cdot (D\underline{\nabla}\rho_A) \tag{8}$$

which is the governing differential equation for the diffusion of an organic penetrant into a polymer.

PROBLEM STATEMENT

Diffusion takes place into a polymer sheet which is initially penetrant-free. At $t = 0$ the penetrant starts to diffuse and the surface is maintained at a constant mass concentration ρ_{A0}. For diffusion of liquid penetrants with good swelling powers, the polymer can stay glassy only for very small concentrations. Therefore, the amount of penetrant in the glassy region is neglected. For a coordinate system shown in Fig. 1, the governing differential equation, (8), together with the initial and boundary conditions take the form

$$\frac{\partial \rho_A}{\partial t} = D\frac{\partial^2 \rho_A}{\partial x^2} - v_x^0 \frac{\partial \rho_A}{\partial x} \tag{9}$$

$$\rho_A = 0 \quad \text{at} \quad t = 0, \text{ for all } x \tag{10}$$

$$\rho_A = \rho_{A0} \quad \text{at} \quad x = 0, \text{ for } t > 0 \tag{11}$$

$$\rho_A = \rho_{As} \quad \text{at} \quad x = s(t), \text{ for } t > 0 \tag{12}$$

Boundary Condition at the Moving Interface

When (9) is multiplied by dx and integrated from 0 to $s(t)$, the result is

$$\int_0^{s(t)} \frac{\partial \rho_A}{\partial t}\,dx = \left(D\frac{\partial \rho_A}{\partial x}\right)_{x=s(t)} - \left(D\frac{\partial \rho_A}{\partial x}\right)_{x=0} - v_x^0(\rho_{As} - \rho_{A0}). \tag{13}$$

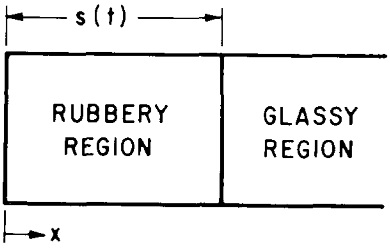

Fig. 1.

Application of Leibnitz's rule to the left side of (13) gives

$$\frac{d}{dt}\int_0^{s(t)} \rho_A dx - \rho_{As}\frac{ds}{dt} = \left(D\frac{\partial \rho_A}{\partial x}\right)_{x=s(t)} - \left(D\frac{\partial \rho_A}{\partial x}\right)_{x=0} - v_x^0(\rho_{As} - \rho_{A0}). \tag{14}$$

The use of the equation for the conservation of mass in the form

$$\frac{d}{dt}\int_0^{s(t)} \rho_A dx = -\left(D\frac{\partial \rho_A}{\partial x}\right)_{x=0} + v_x^0 \rho_{A0} \tag{15}$$

simplifies (14) to

$$D\frac{\partial \rho_A}{\partial x} + \rho_{As}\frac{ds}{dt} - v_x^0 \rho_{As} = 0 \text{ at } x = s(t), \tag{16}$$

which is the boundary condition at the moving interface.

SOLUTION OF THE MODEL EQUATION

Introduction of the dimensionless quantities

$$\theta = \frac{\rho_A - \rho_{A0}}{\rho_{As} - \rho_{A0}}, \tag{17}$$

$$\tau = \frac{(v_x^0)^2 t}{4D}, \tag{18}$$

$$q = \frac{v_x^0 x}{4D}, \tag{19}$$

and

$$\beta = \frac{\rho_{A0}}{\rho_{As}} - 1 \tag{20}$$

reduces (9), (11), (12) and (16) to

$$\frac{\partial \theta}{\partial \tau} + \frac{\partial \theta}{\partial q} = \frac{1}{4}\frac{\partial^2 \theta}{\partial q^2}, \tag{21}$$

$$\theta = 0, \text{ at } q = 0 \tag{22}$$

$$\theta = 1, \text{ at } q = q_s \tag{23}$$

$$\frac{1}{\beta}\frac{dq_s}{d\tau} = \frac{1}{\beta} + \frac{1}{4}\frac{\partial \theta}{\partial q}, \text{ at } q = q_s \tag{24}$$

where

$$q_s = \frac{v_x^0 s}{4D}. \tag{25}$$

Hitherto, no known analytical solution to (21) with the boundary conditions defined by (22–24) exists. Since the glassy core is assumed to be completely unpenetrated at any instant, a discontinuous jump in the concentration profile occurs at the moving boundary and this causes an additional difficulty.

A method suggested by Meyer [10, 11] which is a combination of the method of lines and the method of invariant embedding is modified and adopted for the solution of the problem. The method of lines converts a partial differential equation to a set of ordinary differential equations by discretizing the time coordinate. The method of invariant embedding, on the other hand, converts a boundary value problem to an initial value problem without the requirement of shooting. Therefore, when these two methods are combined and applied to a partial differential equation, a set of ordinary differential equations are obtained as initial value problems and these can be simultaneously integrated with any one of the well-known methods such as the fourth-order Runge-Kutta method.

The governing differential equation, (21), is discretized in time using the backward difference

$$\frac{\theta_n - \theta_{n-1}}{\Delta\tau} + \frac{d\theta_n}{dq} = \frac{1}{4}\frac{d^2\theta_n}{dq^2}. \tag{26}$$

Meyer [10, 11] states that the time-discretized differential equation can be expressed as a set of two first-order ordinary differential equations with variable coefficients in the form

$$\frac{d\theta_n}{dq} = H_1(q)\theta_n + H_2(q)w + H_3(q) \tag{27}$$

and

$$\frac{dw}{dq} = H_4(q)\theta_n + H_5(q)w + H_6(q), \tag{28}$$

where w is a dummy dependent variable.

For the specific problem at hand, (27) and (28) take the form

$$\frac{d\theta_n}{dq} = 4\theta_n + 4w, \tag{29}$$

$$\frac{dw}{dq} = \frac{\theta_n}{\Delta\tau} - \frac{\theta_{n-1}}{\Delta\tau}. \tag{30}$$

Note that (29) and (30) satisfy (26).

The Riccati transformation is applied to the dependent variable θ in the form

$$\theta = R(q)w + f(q), \tag{31}$$

where R and f are dummy functions of the dimensionless distance, q. Use of (30) and (31) in (29) leads to

$$\left(\frac{dR}{dq} + \frac{R^2}{\Delta\tau} - 4R - 4\right)w + \frac{df}{dq} + \frac{Rf}{\Delta\tau} - \frac{R\theta_{n-1}}{\Delta\tau} - 4f = 0, \tag{32}$$

which is an identity in terms of the dependent variable w. Hence, the coefficients of the powers of w must vanish to give

$$\frac{dR}{dq} = -\frac{R^2}{\Delta t} + 4R + 4 \tag{33}$$

and

$$\frac{df}{dq} = \frac{R}{\Delta \tau}(\theta_{n-1} - f) + 4f. \tag{34}$$

In order to solve the above equations, initial conditions should be known. At $q = 0$, (31) becomes

$$\theta(0) = R(0)w(0) + f(0) = 0. \tag{35}$$

(35) must be valid whatever the functional form of w is. This is satisfied if

$$R(0) = 0 \tag{36}$$

and

$$f(0) = \theta(0) = 0. \tag{37}$$

Substitution of (29) into the time-discretized form of (24) gives the condition at the moving boundary as

$$w(q_s) = \frac{1}{\beta}\frac{(q_s)_n - (q_s)_{n-1}}{\Delta \tau} - \frac{1}{\beta} - 1. \tag{38}$$

Use of this result along with the Riccati transformation, (31), leads to

$$R(q_s)\left[\frac{1}{\beta}\frac{(q_s)_n - (q_s)_{n-1}}{\Delta \tau} - \frac{1}{\beta} - 1\right] + f(q_s) - 1 = 0. \tag{39}$$

Note that (33) is in the form of a Riccati equation and the solution is

$$R = \frac{c_2 \exp(c_1 q) - c_1 \exp(c_2 q)}{\exp(c_1 q) - (c_1/c_2)\exp(c_1 q)} \tag{40}$$

where

$$c_1 = 2\left[1 + \sqrt{1 + \frac{1}{\Delta \tau}}\right] \tag{41}$$

$$c_2 = 2\left[1 - \sqrt{1 + \frac{1}{\Delta \tau}}\right] \tag{42}$$

Hence, only (34) is solved numerically using the fourth-order Runge-Kutta method.

Once R and f are determined, the position of the moving boundary q_s, is computed as the first positive root of (39). For this purpose the modified bisection method is used.

To calculate the concentration profile, (31) is rearranged in the form

$$w = \frac{\theta_n - f}{R}. \tag{43}$$

Use of (43) in (29) yields

$$\frac{d\theta_n}{dq} = 4\left(\frac{\theta_n - f}{R} + \theta_n\right). \tag{44}$$

The initial condition for this equation is given by (23). The dimensionless concentration profile θ_n is obtained as a function of the dimensionless distance q by the integration of (44) from q_s to 0 using the fourth-order Runge-Kutta method.

The weight gain per unit cross-sectional area M, can be determined from the integration of the concentration profile over the thickness of the rubbery region as

$$M = \int_0^{s(t)} \rho_A dx. \tag{45}$$

In terms of the dimensionless quantities, (45) takes the form

$$M^* = \left(\frac{1+\beta}{\beta}\right) q_s - \int_0^{q_s} \theta dq, \tag{46}$$

where the dimensionless weight gain, M^*, is defined as

$$M^* = M\left[\frac{v_x^0}{4(\rho_{A0} - \rho_{As})D}\right]. \tag{47}$$

The second term on the right side of (46) is numerically calculated by the 15-point Gauss-Legendre quadrature.

Calculations are carried out by using the Burroughs B–6900 computer. The processing time for $\Delta q = \Delta\tau/20$ and 15 time steps is approximately four minutes. Details of the calculations and the computer program are given elsewhere [9].

RESULTS AND CONCLUSIONS

The magnitude of the dimensionless time τ, defined as $(v_x^0)^2 t/4D$, is strongly dependent on v_x^0/D which in turn depends on the characteristics of the specific polymer–penetrant system. Since $v_x^0 \ll D$ and $v_x^0 \gg D$ for Case I and Case II diffusion mechanisms, respectively, it is possible to predict the diffusion behavior from the solution of the model equation for different values of τ.

The weight gain and the boundary position data are obtained from numerical calculations

Table 2. Regression results of dimensionless weight gain for $\beta = 1.0$

	$M^* = k_1\tau^n$		$M^* = a_1\sqrt{\tau} + b_1$	
τ	k_1	n	a_1	b_1
1×10^{-4}—15×10^{-4}	1.767	0.600	0.676	19.38
1×10^{-3}—15×10^{-3}	1.632	0.619	2.764	0.666
1×10^{-2}—15×10^{-2}	1.617	0.632	0.825	1.148
1×10^{-1}—15×10^{-1}	1.929	0.751	0.795	1.148

Table 3. Regression results of dimensionless boundary position for $\beta = 1.0$

	$q_s = k_2\tau^n$		$q_s = a_2\sqrt{\tau} + b_2$	
τ	k_2	n	a_2	b_2
1×10^{-4}—15×10^{-4}	1.028	0.600	0.337	3.368
1×10^{-3}—15×10^{-3}	0.883	0.619	0.333	1.382
1×10^{-2}—15×10^{-2}	0.808	0.632	0.412	0.574
1×10^{-1}—15×10^{-1}	0.964	0.751	0.397	0.564

and fitted to the expressions represented by

$$M^* = k_1\tau^n \quad \text{or} \quad M^* = a_1\sqrt{\tau} + b_1, \tag{48}$$

$$q_s = k_2\tau^n \quad \text{or} \quad q_s = a_2\sqrt{\tau} + b_2, \tag{49}$$

using a nonlinear regression algorithm. The regression results of the weight gain and the boundary position for $\beta = 1$ are shown in Tables 2 and 3 respectively.

The following observations, for the equation of the form $k\tau^n$, are deduced from an examination of Tables 2 and 3:

1. The exponent of τ is always between 0.5 and 1.0.
2. An increase in τ causes an increase in exponent n (Note that $n = 0.5$ for Case I diffusion and $n = 1$ for Case II diffusion).
3. The exponents of τ in the weight gain and in the boundary position expressions are the same.

The above conclusions are in agreement with experimental observations, as can be seen from Table 4.

To determine the effect of β on the results, calculations are repeated for two more β values and the results are shown in Table 5.

As β decreases, i.e., the concentration at the moving boundary (ρ_{As}) approaches the surface concentration (ρ_{A0}), one can expect the diffusion mechanism to approach Case II and the value of the exponent becomes equal to 1.0. The results shown in Table 5 fit these expectations.

In a practical case, the predictions of the present model can be put into use in the following manner: for several polymer-penetrant systems ρ_{As} is correlated in terms of the glass transition temperature T_g. Thus ρ_{As} can be predicted from a known value of T_g, v_x^0 can be obtained from rate of swelling data, and D from diffusivity data. With the known values of ρ_{A0}, ρ_{As}, v_x^0, and

Table 4. Experimental diffusion data for various polymer—penetrant systems

Polymer	Penetrant	Temperature (°C)	Value of n For M^*	Value of n For q_s	Ref.
Medium crosslinked epoxy	Methylene chloride	25	0.5	0.5	12
High crosslinked epoxy	Methylene chloride	25	1.0	1.0	12
Medium crosslinked epoxy	Benzene	25	1.0	1.0	12
Medium crosslinked epoxy	MEK	25	N.R.	0.58	12
Medium crosslinked epoxy	Trichloroethylene	25	N.R.	0.66	12
P.M.M.A.	Methanol	24	1.0	1.0	13
P.M.M.A.	Methanol	62	0.65	0.65	13

Note: N.R. stands for "not reported".

Table 5. Calculated values of the exponent of τ in the equation $k\tau^n$ using regression analysis

	n for q_s			n for M^*		
τ	$\beta = 0.2$	$\beta = 1.0$	$\beta = 5.0$	$\beta = 0.2$	$\beta = 1.0$	$\beta = 5.0$
1×10^{-4}—15×10^{-4}	0.617	0.599	0.535	0.617	0.599	0.535
1×10^{-3}—15×10^{-3}	0.650	0.619	0.549	0.650	0.619	0.549
1×10^{-2}—15×10^{-2}	0.692	0.632	0.588	0.692	0.632	0.588
1×10^{-1}—15×10^{-1}	0.812	0.751	0.683	0.812	0.751	0.683

D one can calculate β and τ for various lengths of processing time. The weight gain and boundary position values can then be calculated from (48, 49) using the predicted values of a, b, k, and n.

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