

# Diluent Diffusion in Polymer-Diluent Systems Near $T_g$ : Migration of Phthalic Esters from PVC to Water

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## Synopsis

A new mathematical model is presented for the description of certain types of diluent diffusion (migration) through diluent-polymer systems. The model describes anomalous diluent transport into a container of finite volume, and it incorporates mass transfer limitations at the polymer/extractant interface. The extractant is assumed to diffuse slowly or negligibly into the polymer. The model is applied to experimental data obtained with two plasticizers, di(2-ethyl-*n*-hexyl) phthalate and benzyl butyl phthalate, migrating from poly(vinyl chloride) to water.

## INTRODUCTION

Considerable research interest has been shown in recent years in the phenomena and mechanisms underlying the transport of residual monomers and additives from polymeric materials into surrounding fluids and solids (food products), because of the potential environmental hazard and toxicity of these additives.<sup>1,2</sup>

Diffusion of small molecules through polymers can, in certain cases, be explained in terms of Fick's law describing the flux of the diffusing species per unit area as a function of its concentration gradient. However, the usual assumptions involved in the treatment of diffusion behavior in many engineering problems may not be applicable in most polymer-diluent systems due to the structural characteristics of the polymer and the possibility of occurrence of state transitions during the diffusion process. This is the case with the phenomenon of migration of plasticizers from polymers to surrounding fluids, especially when this diffusional release occurs near the glass transition of the polymer/diluent system.<sup>3</sup>

## Non-Fickian Mechanisms

There are numerous types of deviations from Fickian behavior, and Fujita<sup>4</sup> has summarized a representative sample. These include permeation curves which are not linear in the region of small  $t^{1/2}$  values, inflection points in permeation curves, intersection of sorption and desorption curves which have coincidental initial slopes but which slopes do not coincide over the entire region of  $t^{1/2}$  in paired experiments, and permeation curves obtained by varying sample

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thickness, which cannot be reduced to a single curve when plotted versus  $t^{1/2}/l$ .

Vrentas et al.<sup>5</sup> have tried to quantify the conditions under which such non-Fickian behavior can be expected, by introducing a diffusional Deborah number which compares the relaxational and diffusional times characteristic of a mass transport experiment. When a diluent molecule enters the polymer matrix, its movement is restricted by small segment motion of the polymer chains leading only to an "apparent" equilibrium; gradually as larger segmental motion is realized, a final equilibrium is achieved.

Joshi and Astarita<sup>6</sup> have shown that the diffusional and relaxational phenomena lead to a coupled problem between the concentration and activity of a diluent, and only in certain limiting cases can the diffusion and relaxation mechanisms be separated. Ensore et al.<sup>7</sup> demonstrated this experimentally by judicious choice of sample size. By using small (submicron) spheres of polystyrene they found that Fickian diffusion was the controlling mechanism, while with large ( $\sim 200 \mu\text{m}$ ) spheres the relaxation mechanism was controlling.

The Case II transport model was first advanced by Alfrey et al.<sup>8</sup> to explain extremely non-Fickian behavior in glassy polymers. The conditions which characterize Case II transport include a sharp advancing front separating the glassy region from the rubbery region, as the diluent diffuses through the polymer, a boundary between the glassy and rubbery regions which propagates at a constant rate and diluent flux which is proportional to time.

### Previous Experimental Studies

In addition to theoretical and modeling work on the prediction of additive migration, modes of diffusion, fluxes, etc., there has been a considerable amount of work on experimental studies which address problems related to migration. Most of this work has been done using poly(vinyl chloride) (PVC), polyethylene, and polystyrene.

Numerous experimental studies have been reported in recent years on the migration of plasticizers from PVC by research groups working at Unilever of Hamburg, N.T.U. of Athens, M.I.T., and the University of Saint-Etienne of France. The pioneering work of Figge and his co-workers spans a period of 15 years, addresses the migration of additives and plasticizers through PVC into food simulants and other liquids and has been reviewed in an excellent recent publication.<sup>9</sup> Most of their work has used  $^{14}\text{C}$ - and  $^3\text{H}$ -labeled adjunct substances of PVC and investigated migration to surrounding fluids consisting of a fat simulant (HB 307- $^{14}\text{C}$ , a standard triglyceride mixture) and/or tricaprylin. An attractive feature of this work is the availability of reliable data of concentration profiles of plasticizers and penetrants in PVC which can be used for analysis of proposed mathematical models (see, e.g., Ref. 10).

Other experimental information may be obtained from the studies of Kampaouris et al. (e.g., Ref. 11), Reid et al.,<sup>12,13</sup> who offered also interesting Fickian mathematical models discussing the effect of external mass transfer on diluent migration and release, and from the more recent studies of Messadi et al.<sup>14,15</sup>

## MATHEMATICAL MODELING

The mathematical modelling of migration processes of plasticizers in polymers with or without state transitions is a subject which has attracted only limited attention, possibly because of its physical complexity and the assumptions that are necessary in order to model this problem. A review of this subject was presented by Peppas elsewhere,<sup>3</sup> and a mathematically exact but physically unrealistic model was proposed by Peppas and Ziemiński<sup>16</sup> for solution of the general problem. Important mathematical models have also been proposed by Rudolph,<sup>10,17,18</sup> Frisch,<sup>19</sup> Reid et al.,<sup>13</sup> and Wang et al.,<sup>20</sup> who solved the general migration problem with or without volume expansion due to countercurrent diffusion of the surrounding fluid, and usually with concentration-independent diffusion coefficients.

Here we present a model which can be used to describe certain types of diluent migration from polymer/diluent systems near  $T_g$  under non-Fickian diffusion conditions. It may be used when countercurrent diffusion of the surrounding liquid into the system is slow and does not alter the structure and volume of the slab.

In our model the polymer is treated as a two-state system, the rubbery state and the glassy state. Concentration-dependent diffusion coefficients based on free volume theories and somewhat more complex boundary conditions are utilized. No analytical solutions of the diffusion equations are possible. This necessitates the use of numerical techniques to solve the diffusion equations.

### Physical Description of the System

The physical system consists of a thin film of plasticized polymer immersed in a fluid. The sample thickness is small compared to its length or width (aspect ratio of 100) to insure one-dimensional diffusion. There is slow or negligible countercurrent diffusion of the surrounding fluid (nonpenetrating extractant). Cocurrent diffusion of any additives such as heat stabilizers, flame retardants, antioxidants, etc., is also assumed negligible.

The nonpenetrating extractant is assumed to be well mixed, and the migration process is assumed to be independent of its nature. Initially, the concentration of the plasticizer is such that the polymer is in the rubbery state (i.e., above the glass transition temperature) and the plasticizer is uniformly distributed within the polymer. As plasticizer begins moving out of the film, a glassy-rubbery transition is observed, and a moving front, with velocity  $v$ , separates the outer glassy from the inner rubbery region. The governing diffusion equation in the rubbery region is

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[ D(c) \frac{\partial c}{\partial x} \right] \quad (1)$$

where  $c$  is the concentration of plasticizer,  $D(c)$  is the concentration-dependent diffusion coefficient,  $x$  is the direction of diffusion, and  $t$  is time. In the glassy region we use the transport equation suggested by Alfrey et al.<sup>8</sup>:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[ D(c) \frac{\partial c}{\partial x} - vc \right] \quad (2)$$

The problem is solved for half of the slab and symmetry conditions may be applied. The boundary conditions which apply to both equations depending on the state of the polymer at the particular boundary are

$$\frac{\partial c}{\partial x} = 0 \quad \text{at } x = 0 \quad (3)$$

and

$$D(c_l) \left. \frac{\partial c}{\partial x} \right|_l = k(c_l - c_b) \quad \text{at } x = l \quad (4)$$

where  $k$  is a mass transfer coefficient which may be also written as the ratio of plasticizer diffusion coefficient in water over the thickness of the boundary layer,  $c_b$  is the concentration of diluent (plasticizer) in the nonpenetrating extractant, and  $l$  is the half-thickness of the polymer. As a result of a mass balance of plasticizer in the surrounding fluid (extractant) of finite volume, the following expression is obtained:

$$\frac{\partial c_b}{\partial t} = \frac{A}{V} N_l \quad (5)$$

Here  $V$  is the volume of the surrounding fluid,  $A$  is the area of the film, and  $N_l$  is the flux of plasticizer evaluated at the film surface. Substitution of eq. (4) for the flux in eq. (5) gives

$$\frac{\partial c_b}{\partial t} = \frac{Ak}{V} (c_l - c_b) \quad (6)$$

In eq. (6) two possible solutions can exist depending on the values of  $c_l$  and  $c_b$ . The value of  $c_l$  may be assumed known, since the nature of the nonpenetrating extractant affects the partitioning of plasticizer between the film and the extractant. This is the approach taken by Reid et al.<sup>13</sup> and Rudolph<sup>17</sup> through the use of Nernst partition coefficients. The second possibility is that the value of  $c_b$  be assumed constant and equal either to zero or to the solubility concentration of the plasticizer in the extractant. This latter approach is taken here.

At the interface between the rubbery and glassy regions continuity requires that the fluxes be equal:

$$D_r(c) \left. \frac{\partial c}{\partial x} \right|_{L^-} = D_g(c) \left. \frac{\partial c}{\partial x} \right|_{L^+} - v c_{L^+} \quad (7)$$

Here  $D_r(c)$  and  $D_g(c)$  are the diffusion coefficients in the rubbery and glassy states, respectively, and  $L$  is the position of the glassy/rubbery interface. The diffusion coefficients in both states are of the form

$$D(c) = D_0 f(c) \quad (8)$$

where  $f(c)$  is a dimensionless function of plasticizer concentration. In this case the form of  $f(c)$  is given by eq. (9), by analogy to Fujita's free volume theories,<sup>4</sup>

$$f(c) = \exp[-\alpha(c - \beta)] \quad (9)$$

where  $\alpha$  and  $\beta$  are constants.

The initial condition is uniform concentration of plasticizer throughout the polymer

$$c = c_0, \quad 0 \leq x \leq l, \quad \text{at } t = 0 \quad (10)$$

### Solution of the Diffusion Problem

The differential equations, initial and boundary conditions, and the interface conditions are made dimensionless by defining the following dimensionless groups:

$$\begin{aligned} \Gamma = L/l, \quad \psi = c/c_0, \quad \xi = x/l \\ \tau = D_0 t/l^2, \quad \nu = \nu l/D_0, \quad T = \nu l 2h/(D_r - D_g)f(\psi) \\ \delta = D_g/D_r, \quad \kappa = kl/D_r \quad (11) \end{aligned}$$

Using these groups, eq. (1) becomes

$$\frac{\partial \psi}{\partial \tau} = \frac{\partial}{\partial \xi} \left[ f(\psi) \left[ f(\psi) \frac{\partial \psi}{\partial \xi} \right] \right] \quad (12)$$

and eq. (2) becomes

$$\frac{\partial \psi}{\partial \tau} = \frac{\partial}{\partial \xi} \left[ \delta f(\psi) \frac{\partial \psi}{\partial \xi} - \nu \psi \right] \quad (13)$$

The initial and boundary conditions are

$$\psi = 1, \quad 0 < \xi < 1, \quad \text{at } \tau = 0 \quad (14)$$

$$\frac{\partial \psi}{\partial \xi} = 0 \quad \text{at } \xi = 0 \quad (15)$$

and

$$f(\psi) \frac{\partial \psi}{\partial \xi} = \kappa (\psi_{\xi=1} - \psi_b) \quad \text{at } \xi = 1 \quad (16)$$

At the interface,  $\xi = \Gamma$ ,

$$f(\psi) \frac{\partial \psi}{\partial \xi} \Big|_{\Gamma^-} = \delta f(\psi) \frac{\partial \psi}{\partial \xi} \Big|_{\Gamma^+} - \nu \psi \Big|_{\Gamma^+} \quad (17)$$

Because of the concentration-dependent diffusion coefficient, the boundary conditions, and the interface condition, an analytical solution to the diffusion equations is not possible. Therefore, these equations were written in finite difference form, by converting only the partial derivatives with respect to  $\xi$ . Thus a system of  $n + 2$  first-order linear differential equations in  $\tau$  with  $n + 2$  unknowns was generated, where  $n$  is the number of intervals in the polymer.

The difference equations are presented below. Equation (12) becomes

$$\begin{aligned} \frac{\partial \psi}{\partial \tau} \Big|_i = \psi_{i+1} \left[ \frac{3f(\psi_{i+1}) + f(\psi_{i-1})}{4h^2} \right] + \psi_i \left[ \frac{-4f(\psi_{i+1}) - 4f(\psi_{i-1})}{4h^2} \right] \\ + \psi_{i-1} \left[ \frac{f(\psi_{i+1}) + 3f(\psi_{i-1})}{4h^2} \right] \quad (18) \end{aligned}$$

and eq. (13) gives

$$\frac{\partial \psi}{\partial \tau} \Big|_i = \psi_{i+1} \left[ \frac{3\delta f(\psi_{i+k}) + \delta f(\psi_{i-1}) - 2\nu h}{4h^2} \right] + \psi_i \left[ \frac{-4\delta f(\psi_{i+1}) - 4\delta f(\psi_{i-1})}{4h^2} \right] + \psi_{i-1} \left[ \frac{\delta f(\psi_{i+1}) + 3\delta f(\psi_{i-1}) + 2\nu h}{4h^2} \right] \quad (19)$$

where  $h$  is the interval size. The initial and boundary conditions become

$$\psi_i = 1 \quad (i = 1, 2, \dots, n+1) \quad \text{at } \tau = 0 \quad (20)$$

$$\frac{\partial \psi}{\partial \tau} = \frac{8f(\psi_2)}{4h^2} [\psi_2 - \psi_1] \quad \text{at } \xi = 0 \quad (21)$$

and

$$\frac{\partial \psi_b}{\partial \tau} = \kappa [\psi_{n+1} - \psi_b] \quad \text{at } \xi = 1 \quad (22)$$

Finally the interface condition is

$$\psi_{\Gamma+1} = \psi_{\Gamma-1} - T\psi_{\Gamma} \quad (23)$$

### Results of the Mathematical Modeling

The numerical solution scheme requires the input of several parameters which are characteristic of a particular polymer/plasticizer/extractant system. These values were: zero-concentration limit value of rubbery diffusion coefficient,  $D_r = 1.0 \times 10^{-8}$  cm<sup>2</sup>/s; zero-concentration limit value of glassy diffusion coefficient,  $D_g = 1.0 \times 10^{-13}$  cm<sup>2</sup>/s; velocity of the moving front,  $v = 1.0 \times 10^{-6}$  cm/s; and mass transfer coefficient,  $k = 1.0 \times 10^{-5}$  cm/s. Other parameters used were determined from typical laboratory experimental procedures, i.e., volume of the surrounding fluid of 250 cm<sup>3</sup>, film thickness of 127  $\mu$ m, and film area of 9 cm<sup>2</sup>.

The numerical solution was obtained with the Runge-Kutta method based on Verner's fifth and sixth order pair of formulae.

Figures 1-4 show concentration profiles of diluent in the polymer expressed as normalized concentration,  $c/c_0$ , vs. normalized depth position  $x/l$  for different normalized time  $\tau = Dt/l^2$ . The profiles are for different values of  $\alpha$  and  $\beta$ , the two constants of eq. (9) which describe the dependence of the diffusion coefficient on diluent concentration. As time increases, the concentration profiles become flatter and the dimensionless position of the glass/rubbery front moves inwards as shown in Table I.

The effect of  $\alpha$  on the concentration profiles can be seen by comparing the profiles at constant  $\beta$  (e.g., Figures 1 and 2 or 3 and 4). As  $\alpha$  changes from -1 to 1, the profiles become more distorted at early times; as the polymer becomes more glassy, the effect is reduced. The rate of migration increases with increasing  $\alpha$ ; it also increases with increasing  $\beta$  at  $\alpha = 1$ , but decreases with increasing  $\beta$  at  $\alpha = -1$ .

Of these cases a physically important one is that of  $\alpha = -1$ , where the diffusion coefficient increases with increasing concentration. A plot of the fraction of diluent remaining in the polymer as a function of migration times shows that

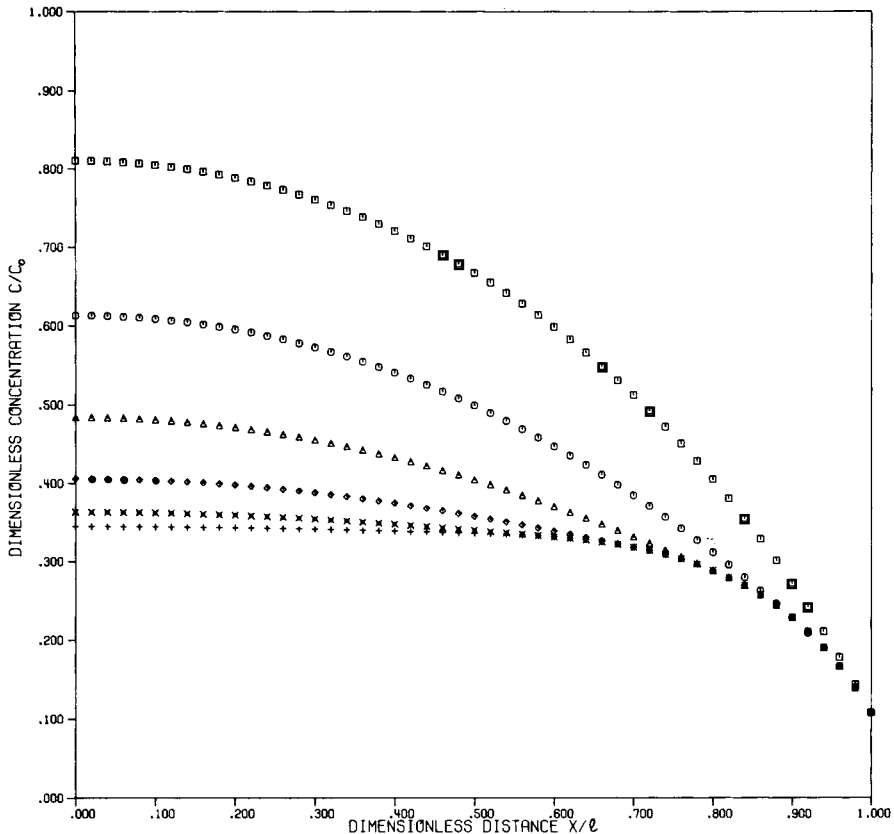


Fig. 1. Dimensionless concentration of diluent in polymer as a function of dimensionless distance. Solution of mathematical model for diffusion coefficient with  $\alpha = -1$  and  $\beta = 0.5$ . Curves are for dimensionless time  $\tau$  of 0.1575, 0.3150, 0.4724, 0.6299, 0.7874, and 0.9949, progressively increasing from the top to the bottom curve.

in all cases the amount released is proportional with time (see Fig. 5). This dependence would be expected for anomalous transport release models for plasticizer migration. Unfortunately, the experimental results presented below are not conclusive enough to suggest whether indeed anomalous (non-Fickian) transport agrees with the proposed models.

## EXPERIMENTAL

### Materials

Experimental studies were carried out with polymer/diluent systems consisting of amorphous poly(vinyl chloride) (PVC), two plasticizers, di(2-ethyl-*n*-hexyl)-phthalate (DEHP) and benzyl butyl phthalate (BBP), and a heat stabilizer (Thermolite 73), at constant temperature with initial concentrations of plasticizer such that the polymer/diluent systems were in the rubbery state, but only slightly above  $T_g$  with respect to the experimental temperature.

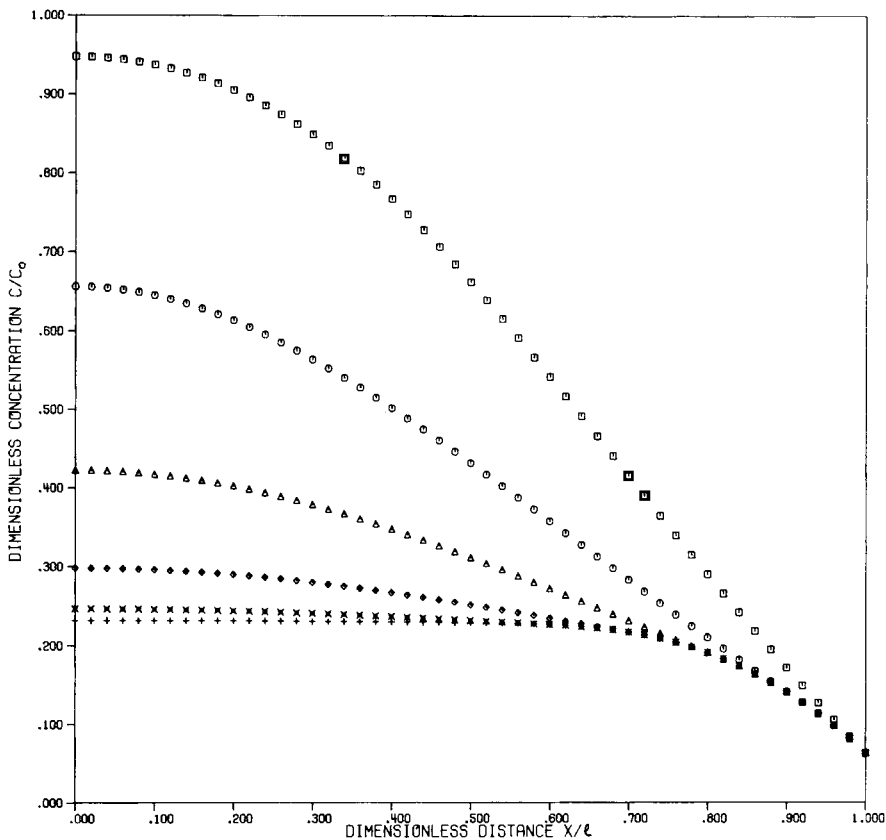


Fig. 2. Dimensionless concentration of diluent in polymer as a function of dimensionless distance. Solution of mathematical model for diffusion coefficient with  $\alpha = 1$  and  $\beta = 0.5$ . Curves are for dimensionless times  $\tau$  of 0.1575, 0.3150, 0.4724, 0.6299, 0.7874, and 0.9449, progressively increasing from the top to the bottom curve.

Poly(vinyl chloride) was obtained from the Firestone Plastics Co., Pottstown, Pa. It was emulsion-polymerized, with  $\bar{M}_n = 94,500$ ,  $\bar{M}_w = 195,200$ , and a polydispersity index of 2.065 as determined by gel permeation chromatography.

The plasticizer DEHP (Aldrich Chemical Co.) had molecular weight of 390.56 daltons, boiling point of 384°C and density of 0.981 g/cm<sup>3</sup>. The plasticizer BBP (Santicizer 160, Monsanto Co.) had molecular weight of 312.35 daltons, boiling point of 370°C, and density of 1.111 g/cm<sup>3</sup>.

Thermolite 73 [dibutyltin-*S, S'*-bis(isooctyl mercaptoacetate)], a heat stabilizer, was obtained from the M&T Chemical Co., Rahway, N.J. Its molecular weight is 608.0 daltons, its density is 1.25 g/cm<sup>3</sup>, and its viscosity at 25°C is 110 cp. It is insoluble in water, and highly soluble in alcohols and hydrocarbons.<sup>21</sup>

### Sample Preparation

The appropriate amounts of PVC, plasticizer, and stabilizer were blended together in a mixing flask using a three-blade, screw-type impeller connected



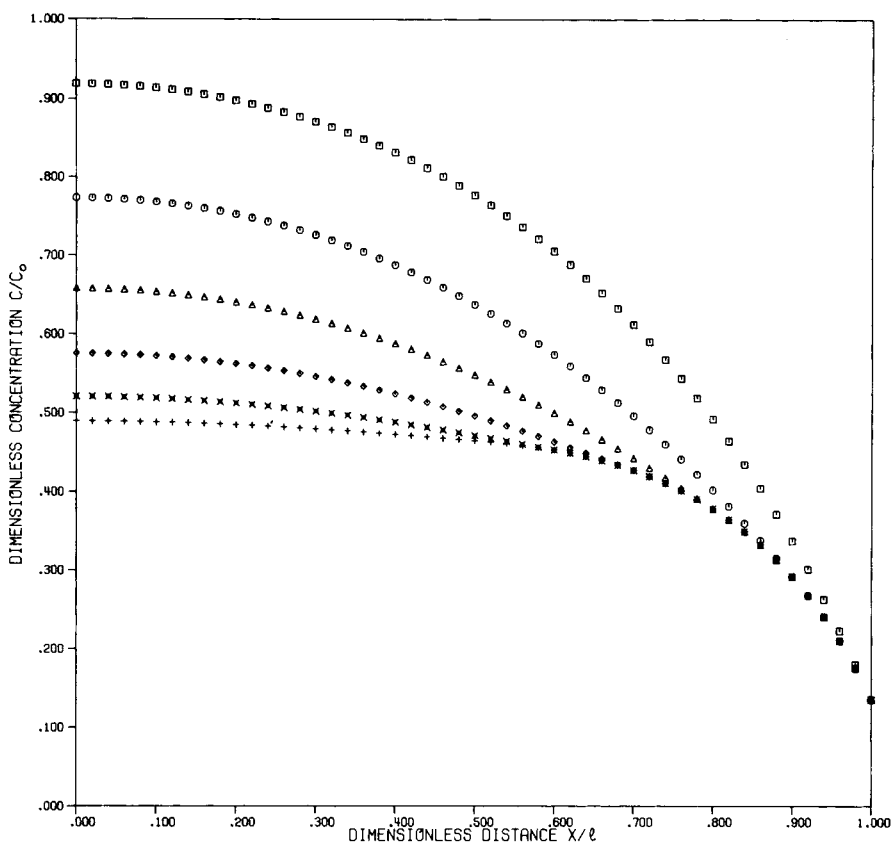


Fig. 3. Dimensionless concentration of diluent in polymer as a function of dimensionless distance. Solution of mathematical model for diffusion coefficient with  $\alpha = -1$  and  $\beta = 1$ . Curves are for dimensionless times  $\tau$  of 0.1575, 0.3150, 0.4724, 0.6299, 0.7874, and 0.9449, progressively increasing from the top to the bottom curve.

to a constant speed of 20 rpm under isothermal mixing conditions. The mixture was then cast into thin sheets in a casting apparatus, at 37°C, and placed in a constant temperature oven for a specified period of time. The processing conditions for the systems studied here were selected based on previous work on the fusion behavior of the same systems by Patterson et al.,<sup>22</sup> who determined the conditions under which full solvation of the polymer particles by the plasticizer would have been achieved.

The sheets were cut in 3 cm  $\times$  3 cm squares and their thickness was measured with a micrometer ( $\pm 12.5 \mu\text{m}$ ). Individual samples were identified by the following code: type of plasticizer (DEHP or BBP), followed by the batch number (I, II, III, etc.) which corresponds to a particular plasticizer concentration and finally the number of the sample (1, 2, 3, etc.). Thus DEHP IV 23 refers to sample number 23 of batch IV having been plasticized with DEHP. In all, 822 samples were prepared, and the samples used in the diffusion experiments were selected on the basis of no more than a 0.001-in. difference in the highest and lowest thickness measurement.

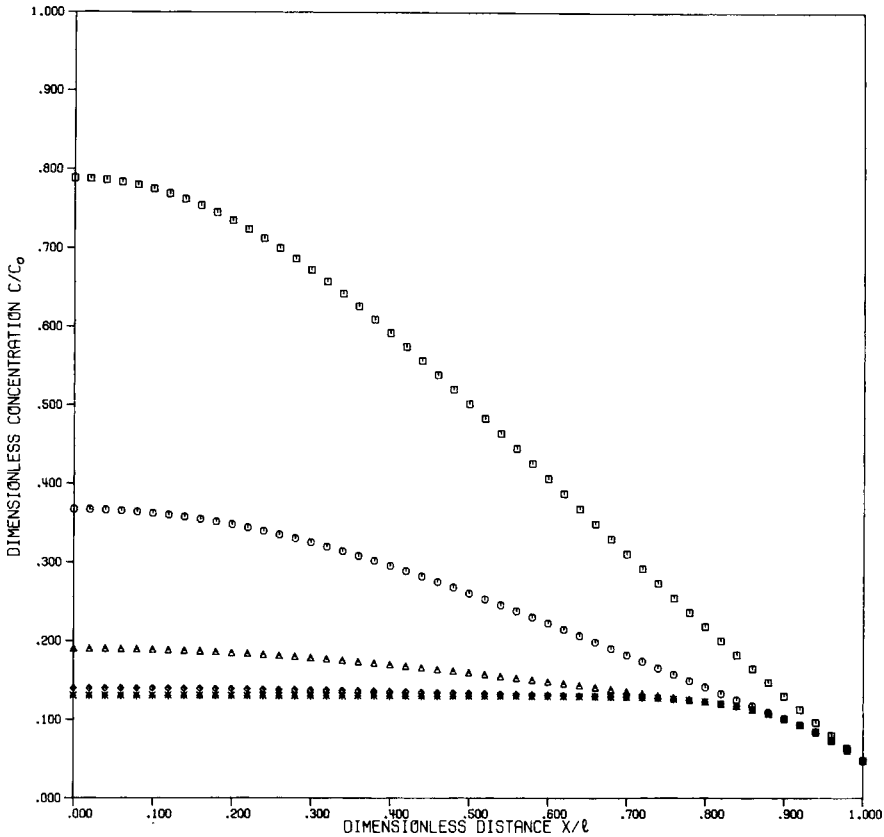


Fig. 4. Dimensionless concentration of diluent in polymer as a function of dimensionless distance. Solution of mathematical model for diffusion coefficient with  $\alpha = 1$  and  $\beta = 1$ . Curves are for dimensionless times  $\tau$  of 0.1575, 0.3150, 0.4724, 0.6299, 0.7874, and 0.9449, progressively increasing from the top to the bottom curve.

The glass transition temperatures of the samples used in this study were determined by differential scanning calorimetry using a DSC-1B (Perkin-Elmer). Thermal and other characteristics of these samples have been discussed exten-

TABLE I  
Dimensionless Position of the Glass/Rubber Interface as a Function of Dimensionless Time

Dimensionless time ( $Dt/l^2$ )	Position of front ( $L/l$ )
0.1575	1.00
0.25	0.9413
0.3150	0.90
0.4724	0.80
0.50	0.7825
0.6299	0.70
0.75	0.6237
0.7874	0.60
0.9449	0.50

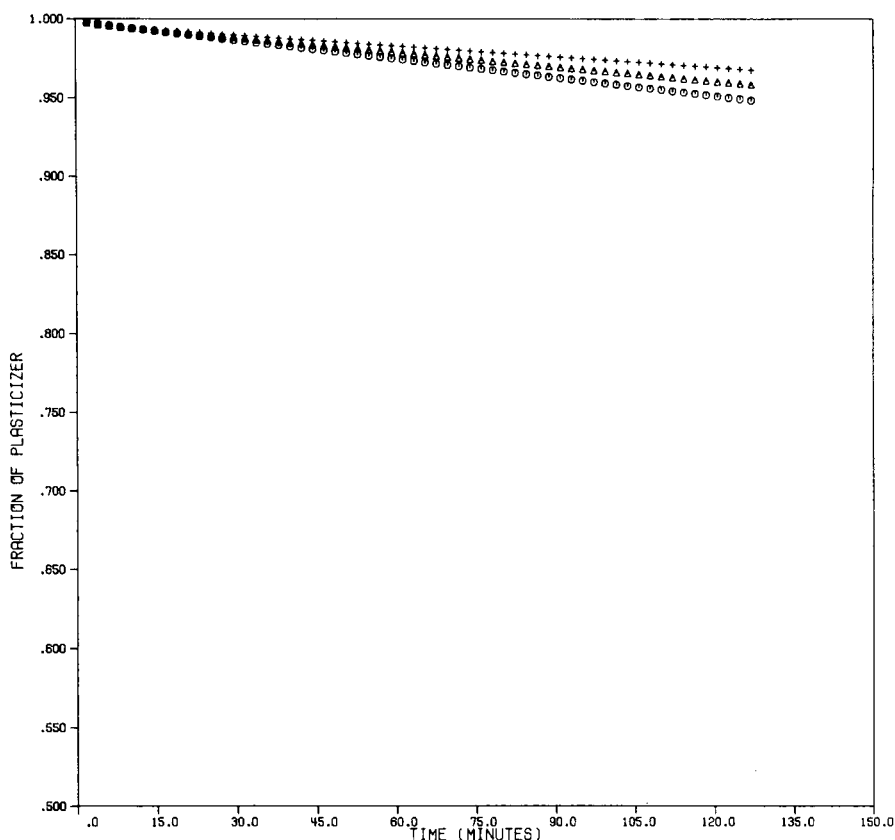


Fig. 5. Weight fraction of plasticizer remaining in polymer as a function of time. Solution of mathematical model for diffusion coefficient with  $\beta = 1$  and  $\alpha$  of  $-1$ ,  $0$ , and  $1$  from top to bottom line.

sively elsewhere.<sup>22</sup> A complete description of the samples prepared is shown in Table II.

### Diffusion Experiments

All diffusion (migration) studies were done in 250 cm<sup>3</sup> Erlenmeyer flasks containing deionized water and maintained at  $30 \pm 1^\circ\text{C}$ . Weight loss of plasticizer was determined by conventional techniques. Also samples of the sur-

TABLE II  
Composition of DEHP/PVC and BBP/PVC Samples

Sample	Polymer (wt %)	Plasticizer (wt %)	Stabilizer (wt %)	Mixing conditions		Fusion conditions		$T_g$ ( $^\circ\text{C}$ )
				(min)	( $^\circ\text{C}$ )	(min)	( $^\circ\text{C}$ )	
DEHP IV	65.34	33.36	1.30	10	35	30	154	24.5
DEHP V	67.44	31.22	1.34	10	35	30	152	26.0
DEHP X	69.23	29.40	1.38	10	40	30	152	27.0
BBP VI	61.57	37.21	1.22	15	25	15	90	26.5
BBP VIII	61.73	37.04	1.23	15	25	15	90	26.5

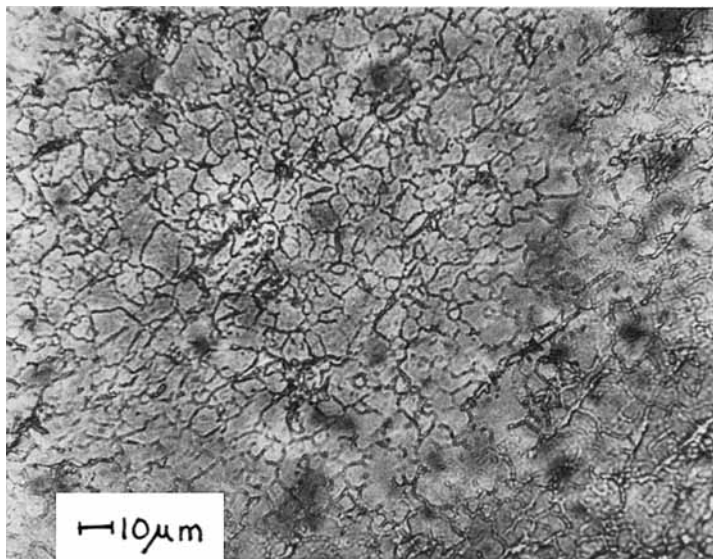


Fig. 6. Transmission photomicrograph (400 X) of a BBP-plasticized PVC sample (37.04 wt % BBP) after immersion in water for 45 days at 30°C.

rounding fluid were analyzed for plasticizer content using a UV-Vis spectrophotometer (Perkin-Elmer, Model 559) at 208 nm for DEHP and 209 nm for BBP.

Transmission micrographs of selected samples were obtained before and after migration using a Leitz microscope and camera apparatus.

## RESULTS AND DISCUSSION

As shown in Table II, all samples prepared had glass transitions below 30°C, the temperature of diffusion studies. Photomicrographs of typical DEHP/PVC

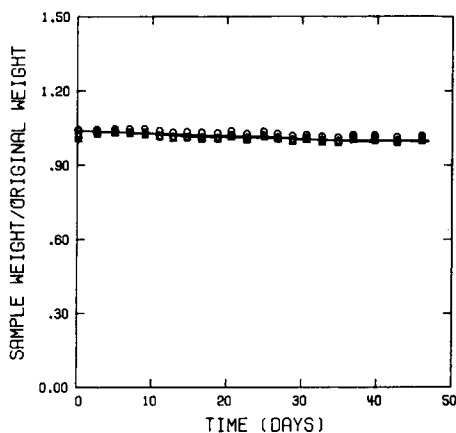


Fig. 7. Weight loss of BBP-plasticized PVC samples (37.21 wt %) as a function of time, upon immersion in water at 30°C: (O) BBP VII 25; (□) BBP VII 30; (Δ) BBP VII 39; (○) BBP VII 47.

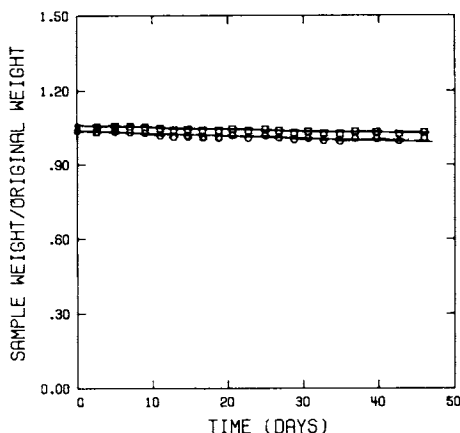


Fig. 8. Weight loss of BBP-plasticized PVC samples (37.21 wt %) averaged by thickness, upon immersion in water at 30°C. Thickness ( $\mu\text{m}$ ): (O)  $79.7 \pm 1.2$ ; (□)  $102.2 \pm 2.0$ .

samples before migration showed no microvoids or defects. It was concluded that good fusion of the plasticizer with the polymer had taken place.

Figure 6 is a photomicrograph of a BBP/PVC sample (37.04 wt %) after immersion in water for 45 days. Intergrain interphases caused by plasticizer removal can be observed on a background of irregular microvoids of 5–15  $\mu\text{m}$ . The size of the PVC particles varies from 2 to 15  $\mu\text{m}$ . Similar findings were observed from all other formulations prepared here. These observations are in agreement with observations by Kampouris et al.<sup>11</sup> of microvoids in these systems as a result of removal of plasticizer. Plots of total weight loss as a function of time show that there was no significant weight change for all samples in water (see, e.g., Figure 7).

The ratio of final thickness to initial thickness for BBP/PVC samples was  $1.02 \pm 0.02$  while the ratio for DEHP/PVC samples was  $0.91 \pm 0.04$ . Thus, there was some shrinkage of the DEHP-plasticized samples during migration, while the BBP samples showed no signs of shrinkage. The level or degree of weight loss appears to be less for thicker samples than for thinner ones. This is more readily seen in Figure 8, where samples of similar plasticizer content have been averaged according to thickness. The effect is more noticeable in the BBP/PVC samples than the DEHP/PVC samples.

A typical plot of experimental results of plasticizer remaining in the polymer as a function of time is shown in Figure 9, for several samples of the same formulation (37.21 wt % BBP in PVC). Over a long period of time the data may be fitted by a straight line. Then diffusion coefficients of various plasticizers may be determined from these results and the proposed model. Unfortunately, the difficulty of obtaining the experimental results presented here precludes any further discussion as to the use of the proposed model or a predictive model for plasticizer migration in water.

The low compatibility of water with PVC indicates that little migration occurs. It appears that not enough water is able to diffuse into the plasticized PVC samples to fill the space left by the departing plasticizer. These unfilled voids eventually collapse leading to an overall shrinkage of the sample.

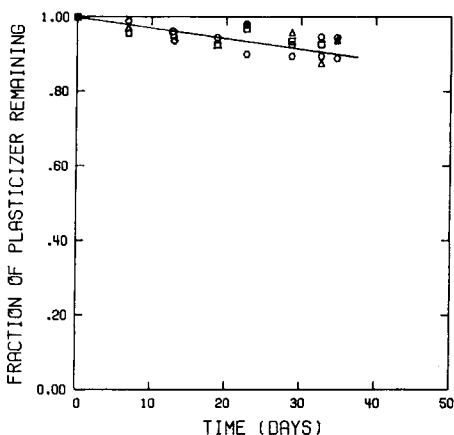


Fig. 9. Fraction of plasticizer remaining in the polymer upon immersion of BBP-plasticized PVC samples (37.21 wt %) in water at 30°C: (○) BBP VII 25; (□) BBP VII 30; (△) BBP VII 39; (◊) BBP VII 47.

## CONCLUSIONS

Experimental studies of plasticizer migration from plasticized-PVC samples near their glass transition temperature show that the release behavior in water is time-dependent. A new mathematical model which considers anomalous transport equations with appropriate boundary conditions is presented, which may be applicable to the analysis of the migration results.

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