

Prediction of the Release Characteristics of Alcohols from EVA Using a Model Based on Fick's Second Law of Diffusion

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ABSTRACT: This study evaluates the use of a simple mathematical model to predict release characteristics of volatile substances from polymer dispensers. The model can be used to simplify the design process of polymer dispensers, which is traditionally done by trial and error. The coefficients of diffusion, D , of four alcohols through EVA disks were determined with the time lag technique. The value of D was used to predict the residual mass of dispensers over time using a model based on Fick's second law of diffusion. Injection-molded dispensers containing 10% alcohol were prepared, and the release of the alcohol were monitored experimentally. The modeled results were compared to the experimental results. A good correlation was found between the predictions and the experimental results. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 806–813, 2002; DOI 10.1002/app.10333

Key words: diffusion; modeling; ethylene–vinyl acetate; controlled release

INTRODUCTION

Polymer matrices can be used for the controlled release of volatile substances into the atmosphere. Examples of applications include insect pheromones,^{1,2} perfumes,³ and volatile corrosion inhibitors.²

If the matrix is a thermoplastic polymer, it can be shaped into a wide range of geometries by the process of injection molding. Not only does this offer a cost effective technique for the mass production of dispensers for volatile substances, but the freedom of design allows dispensers to be made into functional shapes, for example, wristbands containing insect repellent and clip-on dispensers for insect pheromones.

Because the volatile substances (actives) are often expensive to produce, it is important to de-

sign the polymer matrix (dispenser) in such a way that release of the active takes place in a controlled manner. Polymer type, active concentration, and dispenser geometry should allow sufficient concentrations of the active to be released into the atmosphere for it to fulfill its purpose. However, release rates should be kept low enough to conserve the active content of the dispenser for a maximum possible lifetime.

Dispenser development can be done using a trial-and-error process. This requires several iterations of mold making, preparation of different samples, and testing of the release rate. Mold making is a costly and time-consuming process. Release tests are also time consuming and labor intensive if large numbers of samples have to be tested. In addition, if several polymers have to be evaluated, different designs might be required to get the optimum performance from each type of polymer, which means that more than one mold has to be made.

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The objective of this study is to evaluate the accuracy of a mathematical model that can be used to predict the release characteristics of the active from the dispenser. Such a method will allow a larger number of designs to be screened before any molds are made. It can also be used to optimize the design so that the minimum amount of active can be used.

The coefficient of diffusion, D , of the chosen polymer-active combinations were determined using a diffusion cell and the time-lag method. D was substituted into a mathematical model based on Fick's second law of diffusion. The model was used to predict the release characteristics of the active from different dispenser designs. Dispensers with the chosen designs were also prepared by injection molding. The release characteristics were determined experimentally and compared to the predictions obtained from the model.

THEORY

Literature

Many studies on the transport behavior of solvents in polymers have been published. Although some of the studies are aimed at finding a more fundamental explanation of diffusion behavior, others are written against the background of a specific application. Various authors have suggested models that explain diffusion behavior.

Natural rubber is one of the oldest and most commonly used matrices for the release of insect pheromones.⁴ Polyvinyl chloride (PVC) has also been investigated^{5,6} for use as release matrix for pheromones. PVC has the added advantage that release rates can be controlled by varying the plasticizer content. Biopolymers such as starch, whey, and soy proteins were investigated⁷ for the release of pheromones, but were found to be less effective than paraffin waxes. Some authors⁴ have tried to find empirical models with which to predict pheromone release rates of pheromones from dispensers with specific geometries.

The transport of aniline out of EVA beads immersed in water have been studied.^{8,9} A finite element model with a constant coefficient of diffusion and taking swelling into account was used to accurately explain the results. The numerical solution of the finite element model was much more accurate than the analytical solution, which was not valid for solvent concentrations of more than ca. 15%. The transport of toluene into *cis*-

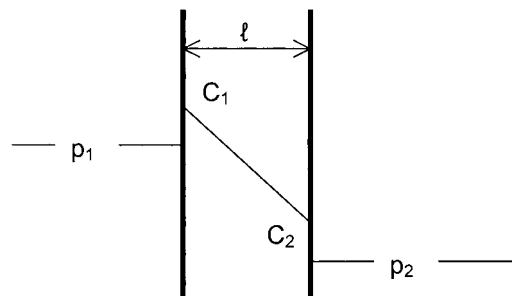


Figure 1 Diagrammatic representation of the cross section of a polymer film in contact with a volatile substance on one surface.

1,4-polyisoprene spheres have been investigated.¹⁰ A model based on Fick's law and taking swelling into account was used to explain the results. The transport of *n*-heptane in and out of thin EVA membranes have been and explained with a Fickian model that takes swelling and shrinking into account.^{11,12} It was found that the numerical model is more accurate than an analytical model that ignores dimensional changes.

Permeation through a Polymer Sheet

Movement of a solvent through a polymer film is called permeation. Permeation consists of three steps¹³: (a) adsorption of the solvent onto the surface of the film; (b) diffusion through the film; and (c) desorption or evaporation from the other surface of the film.

The slowest of the three steps will control the rate at which the solvent moves through the film.

Consider a film that is in contact with a solvent containing gas mixture on the one side (Fig. 1): Where p_1 and p_2 are the partial pressures of the solvent on the up- and downstream sides of the film respectively, C_1 and C_2 are the concentrations of solvent at the upstream and downstream surfaces of the film and l is the film's thickness.

If it is assumed that:

1. Sorption is governed by Henry's law.
2. Diffusion is governed by Fick's second law.
3. The coefficient of diffusion is independent of concentration.
4. The film is initially solvent free.
5. Equilibrium is reached at the solvent rich surface.
6. The concentration at the solvent poor surface is zero.

It can be shown¹⁴ that the amount of solvent that moves through the film, Q , is given as a function of time by the equation:

$$Q = \frac{DC_1}{\ell} \left[t - \frac{\ell^2}{6D} \right] - \left[\frac{2\ell C_1}{\pi^2} \sum_{n=1}^{n=\infty} \frac{(-1)^n}{n^2} \exp\left(\frac{-Dn^2\pi^2 t}{\ell^2}\right) \right] \quad (1)$$

This equation yields a curve (Fig. 2). When t becomes large, the second term in eq. (1) approaches zero. The linear part of the curve is, therefore, described by the equation:

$$Q = \frac{DC_1}{\ell} \left[t - \frac{\ell^2}{6D} \right] \quad (2)$$

If the linear part of the curve is extrapolated back to $Q = 0$, it follows that $t = L$, which is called the lag time. Substituting into the eq. (2) it follows that:

$$0 = \frac{DC_1}{\ell} \left[L - \frac{\ell^2}{6D} \right] \quad (3)$$

which can be solved to show that:

$$D = \frac{\ell^2}{6L} \quad (4)$$

This technique is often used to determine the coefficient of diffusion¹³⁻¹⁵ and is called the time lag test.

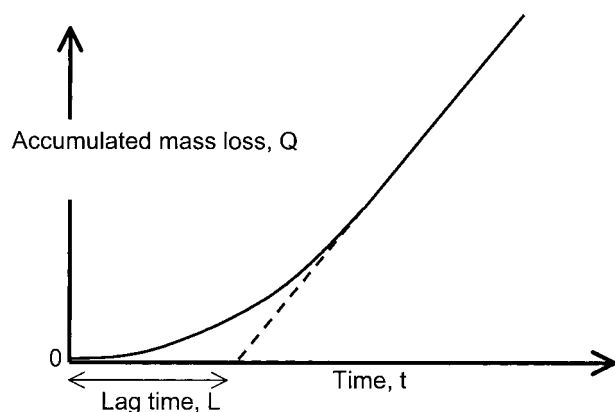


Figure 2 Solvent transmission as a function of time.

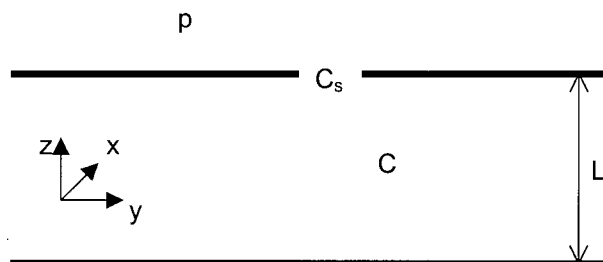


Figure 3 Schematic representation of an infinite flat plate.

The fact that eq. (4) is based on the assumption that D is independent of C (which is known not to be the case for many polymer-solvent systems) means that values of D obtained by this method are often inaccurate and may be too small by a factor of up to 3.¹⁵ However, the time lag test remains a simple and valuable method of determining D , and values are often accurate enough for practical purposes.

Diffusion from a Polymer Matrix

Consider an infinite flat plate with thickness L , solvent concentration C , and surface concentration C_s . The flat plate is, on both sides, in contact with an atmosphere with a partial pressure, p , of the solvent (Fig. 3).

If it is assumed that:

1. Desorption is relatively fast compared to diffusion and governed by Henry's law.
2. Fick's law is valid for the polymer-solvent system at the temperature under consideration.
3. The temperature and the dimensions of the polymer matrix are constant.
4. D is not dependent on C .
5. Diffusion in the x and y directions are of no consequence.
6. The polymer matrix has a uniform solvent concentration of C_0 at zero time.
7. The volume of atmosphere around the polymer matrix is large enough for partial pressure of the solvent to approach zero.

Then the release of the solvent from the polymer will be governed by a simplified version of Fick's second law:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \quad (5)$$

and the following boundary conditions will be valid:

$$\begin{aligned}
 C &= C_0 \text{ at } t = 0 \text{ for } 0 \leq z \leq L \\
 C &= C_s \text{ at } z = 0 \text{ for } t > 0 \\
 C &= C_s \text{ at } z = L \text{ for } t > 0
 \end{aligned}$$

The solution for this differential equation and boundary conditions is known¹⁶ to be:

$$N_z = \frac{4D}{L} (C_s - C_0) \sum_{n=1}^{n=\infty} \left[\cos\left(\frac{\pi n z}{L}\right) \exp\left(\frac{-\pi^2 n^2 t D}{L^2}\right) \right] \tag{6}$$

where $n = 1, 3, 5, 7 \dots$ and N_z is the solvent flux at the horizontal plain running through z .

Because diffusion is slow compared to desorption, and p approaches zero, it follows from Henry's law that $C_s = 0$ at $t > 0$.

Solving the equation for $z = 0$ and $z = L$, the following is obtained:

$$\begin{aligned}
 N_L = -N_0 &= \frac{4DC_0}{L} \left[\exp\left(\frac{-\pi^2 t D}{L^2}\right) \right. \\
 &\quad \left. + \exp\left(\frac{-9\pi^2 t D}{L^2}\right) + \exp\left(\frac{-25\pi^2 t D}{L^2}\right) + \dots \right] \tag{7}
 \end{aligned}$$

The diffusion in a finite polymer matrix with a flat geometry of area A , can be approximated by the solution for an infinite flat plate. The mass of the polymer matrix (including the solvent), M , will decrease from an original mass, M_0 . The rate of mass loss will be equal to the flux from both the polymer matrix's surfaces.

Therefore:

$$\frac{dM}{dt} = -A([N_L] + [N_0]) = -2AN_L \tag{8}$$

$$\begin{aligned}
 dM &= -\left(\frac{8ADC_0}{L}\right) \\
 &\quad \times \left[\exp\left(\frac{-\pi^2 t D}{L^2}\right) + \exp\left(\frac{-9\pi^2 t D}{L^2}\right) + \right. \\
 &\quad \left. \exp\left(\frac{-25\pi^2 t D}{L^2}\right) + \dots \right] dt \tag{9}
 \end{aligned}$$

It is known that:

$$\int \exp(bx) dx = \frac{1}{b} \exp(bx) + k \tag{10}$$

Thus:

$$\begin{aligned}
 \int_{M_0}^M dM &= \int_0^t -\left(\frac{8ADC_0}{L}\right) \\
 &\quad \times \left[\exp\left(\frac{-\pi^2 t D}{L^2}\right) + \exp\left(\frac{-9\pi^2 t D}{L^2}\right) + \right. \\
 &\quad \left. \exp\left(\frac{-25\pi^2 t D}{L^2}\right) + \dots \right] dt \tag{11}
 \end{aligned}$$

Solving this integral equation for M yields:

$$\begin{aligned}
 M - M_0 &= -\left(\frac{8ADC_0}{L}\right) \\
 &\quad \times \left[\left(\frac{-L^2}{\pi^2 D}\right) \left(\exp\left(\frac{-\pi^2 t D}{L^2}\right) - \exp(0)\right) \right. \\
 &\quad \left. + \left(\frac{-L^2}{9\pi^2 D}\right) \left(\exp\left(\frac{-9\pi^2 t D}{L^2}\right) - \exp(0)\right) \right. \\
 &\quad \left. + \left(\frac{-L^2}{25\pi^2 D}\right) \left(\exp\left(\frac{-25\pi^2 t D}{L^2}\right) - \exp(0)\right) + \dots \right] \tag{12}
 \end{aligned}$$

$$\begin{aligned}
 M &= M_0 - \left(\frac{8ADC_0}{L}\right) \left(\frac{-L^2}{\pi^2 D}\right) \\
 &\quad \times \left[\left(\exp\left(\frac{-\pi^2 t D}{L^2}\right) - 1\right) \right. \\
 &\quad \left. + \frac{1}{9} \left(\exp\left(\frac{-9\pi^2 t D}{L^2}\right) - 1\right) \right. \\
 &\quad \left. + \frac{1}{25} \left(\exp\left(\frac{-25\pi^2 t D}{L^2}\right) - 1\right) + \dots \right] \tag{13}
 \end{aligned}$$

$$\begin{aligned}
 M &= M_0 \\
 &\quad + \frac{8ALC_0}{\pi^2} \left[\left(\exp\left(\frac{-\pi^2 t D}{L^2}\right) - 1\right) \right. \\
 &\quad \left. + \frac{1}{9} \left(\exp\left(\frac{-9\pi^2 t D}{L^2}\right) - 1\right) \right. \\
 &\quad \left. + \frac{1}{25} \left(\exp\left(\frac{-25\pi^2 t D}{L^2}\right) - 1\right) + \dots \right] \tag{14}
 \end{aligned}$$

The larger the number of terms in the series used, the more accurate the solution for M will be.

Table I Time Lag Test Results

Solvent	Number of Samples	Average D mm ² /h	Standard Deviation mm ² /h	Standard Deviation % of D
1-Propanol	5	13.22×10^3	0.55×10^3	4.2
1-Butanol	9	11.54×10^3	0.82×10^3	7.1
1-Hexanol	8	8.22×10^3	0.30×10^3	3.7
1-Octanol	5	6.16×10^3	0.41×10^3	6.6

EXPERIMENTAL

Materials

Ethylene–vinyl acetate copolymer (EVA) was used as the polymer matrix in this study. EVA is a branched random copolymer produced by high-pressure radical polymerization. The EVA used in this study was Elvax 260 from Du Pont. It contains 28% vinyl acetate, and has a melt flow index of 6 g/10 min at 190°C and 2.16 kg. The alcohols 1-propanol, 1-butanol, 1-hexanol and 1-octanol were chosen as model actives in this study. All solvents were obtained from Saarchem, except for 1-hexanol, which was obtained from Merck. All solvents were CP grade; except for 1-butanol which was AR grade.

Apparatus

An Engel 3020 injection-molding machine with 800 kN clamping force was used to prepare disks for the time lag tests as well as polymer dispensers for the release tests. It has four temperature zones that were set to 60, 70, 80, and 90°C, respectively. Molding pressure of ca. 12 bar was used and the samples were cooled for 25 s in a mold with a temperature of ca. 25°C.

The thickness of the EVA disks was measured with a Mitutoyo digital micrometer with an accuracy of 1 μ m.

Diffusion cells were used for the time lag tests. The cells consisted of an aluminum base cup, a rubber O-ring, aluminum sealing ring, and an aluminum top. The O-ring fits on top of the base cup. The polymer disk is placed on top of the O-ring after the base cup is filled with the solvent. The sealing ring is then placed on top of the disk to keep it in place, and lastly, the top is screwed tightly onto the base cup to ensure that the whole cell is sealed. The solvent can only escape by permeating through the polymer disk.

All samples used in the release tests were weighed on a calibrated Satorius Research balance with an accuracy of 0.1 mg.

Method

For the time lag tests, approximately 20 mL of solvent was placed in each of the diffusion cells. An injection-molded EVA disk, ca. 3-mm thick and 67.5 mm in diameter was fixed to the top of the diffusion cell. The cells were placed on an open shelf in a laboratory with the temperature controlled at $23 \pm 2^\circ\text{C}$. Care was taken to ensure that the cells were standing in a location where they were not exposed to air movement that might affect the rate of diffusion. However, the area was well ventilated to prevent a buildup of solvent in the atmosphere. The cells were weighed at regular intervals. The coefficient of diffusion was determined using the method described in the theoretical section. The data was plotted in the shape of Figure 2. The lag time was determined graphically and eq. (4) was used to calculate D .

To prepare samples for the release tests, EVA granules were mixed with approximately 10% by mass of the different alcohols. The mixture was sealed in a glass jar and left to stand at room temperature until the polymer had absorbed most of the solvent. The mixture was then injection molded into two different shapes. The first was a round disk with a diameter of 67.5 mm and a thickness of 3 mm. The second was a square disk with a 59-mm side length and a thickness of 2 mm. The square disk had rounded corners with a radius of 2.5 mm. Immediately after injection molding, the disks were sealed in glass jars and left to stand overnight at 23°C. After ca. 24 h the disks were removed from the jars and placed on a steel grid in a temperature controlled laboratory. They were weighed immediately and thereafter at regular intervals. Weighing was continued until the rate of mass loss approached zero.

The diffusion model was based on eq. (14), which can be rewritten in the following form to predict the residual mass, M :

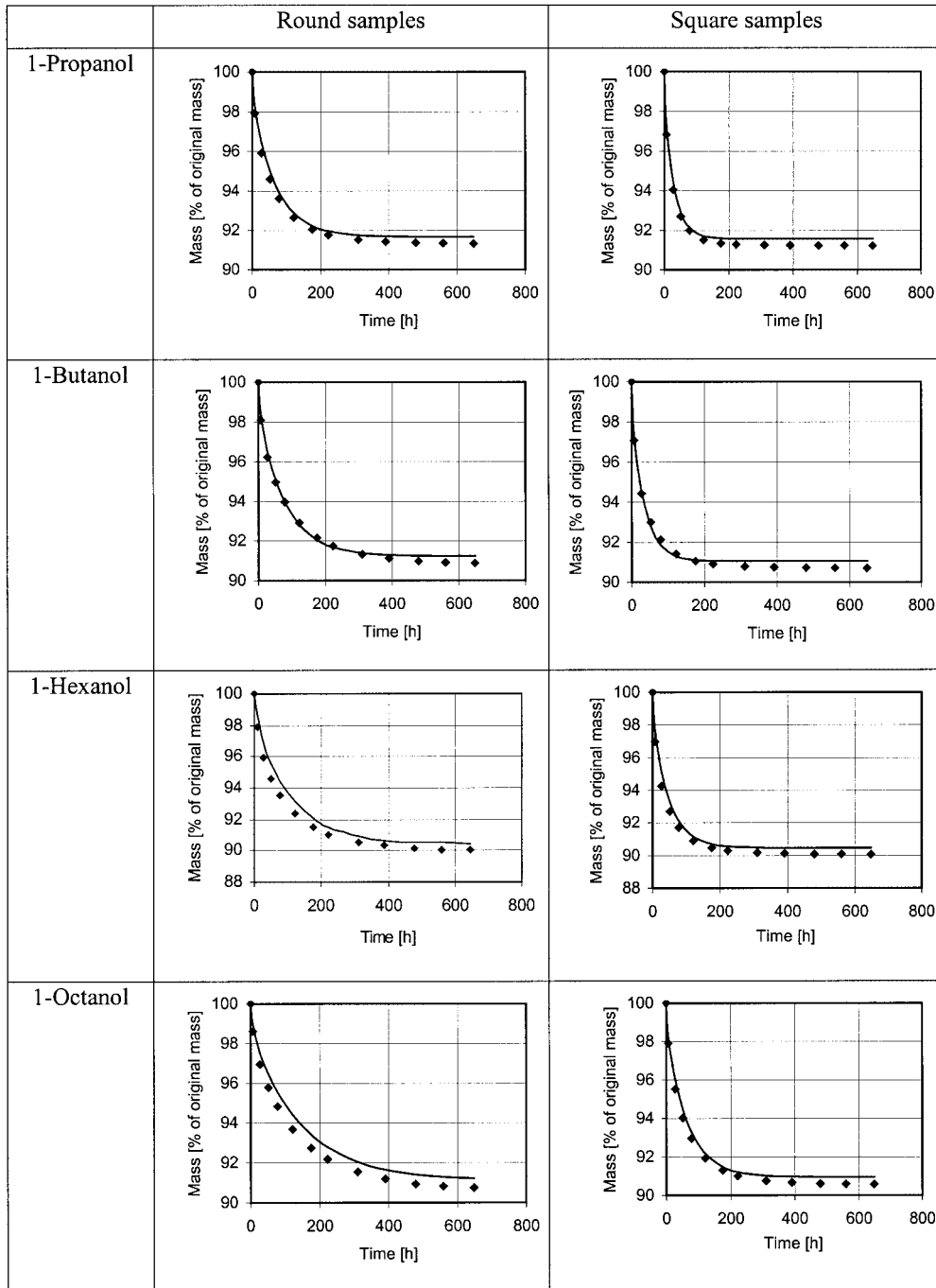


Figure 4 Residual mass [where \blacklozenge are the experimental results and— are the predicted results].

$$M = M_0 + \frac{8ALC_0}{\pi^2} \times \left[\left(\exp\left(\frac{-\pi^2 tD}{L^2}\right) - 1 \right) + \frac{1}{9} \left(\exp\left(\frac{-9\pi^2 tD}{L^2}\right) - 1 \right) + \frac{1}{25} \left(\exp\left(\frac{-25\pi^2 tD}{L^2}\right) - 1 \right) + \dots \right] \quad (15)$$

M_0 was the starting mass of the test piece. C_0 was the original concentration of solvent in the disk, as determined from the final mass of the disks used in the release tests. The area A was calculated as two times the surface area of the disks. The areas of the sides of the disks were assumed to be negligible. L is the thickness of the disks, t is time elapsed since the beginning of the tests, and D is the coefficient of diffusion for the solvent under investigation as determined with the time lag tests.

RESULTS AND DISCUSSION

The results obtained for the time lag tests are shown in Table I.

The standard deviation seems high, but this is probably due to the small number of samples tested.

Water absorption from the air was a major concern during both the time lag tests and the release tests. To quantify the effect of water absorption, control samples without any active were included in both the time lag and release tests. It was found that water absorption accounted for less than 1% of the observed changes in sample mass. For this reason the effect of water absorption caused by changes in relative humidity was ignored in all experiments.

Figure 4 contains the graphical result plotted as residual mass as a percentage of starting mass vs. time elapsed. The release curves predicted by the model are shown on the same graphs as solid lines.

The models gave good predictions of residual mass in all cases. It never diverged more than 1% from the experimental result. Because solvent loadings of ca. 10% was used, it can be argued that the model has an inaccuracy of 10%.

The experimental release rate was faster than predicted in almost all cases. This was expected, because the model used does not consider swelling. It has been shown^{7,8,10,11} that the effective

rate of diffusion is higher than predicted, while there is sufficient solvent trapped in the matrix to increase the amount of free volume and thus the rate of diffusion. For this reason the model is expected to be more accurate at lower solvent loadings and less accurate at higher loadings. Modifying the model to account for swelling will definitely increase the accuracy.

The result for 1-propanol and 1-butanol seems to be more accurate than that for 1-hexanol and 1-octanol. This is probably due to inaccuracies in the determination of D , and not characteristic of the model. In all cases, the model gave a better prediction of the result of the square samples than the round samples. This is probably because the square disks are thinner. Thus, the area on the sides of the samples (which were ignored in the model) forms a smaller percentage of the total area of the disks.

CONCLUSION

The proposed model predicted the residual mass to within 10% of the actual value. The experimental release tests showed a slightly higher release rates than predicted. This was expected, because the assumption that the coefficient of diffusion is independent of concentration was known to be inaccurate. For this reason the proposed model will be less accurate at higher solvent loadings, and more accurate at lower solvent loadings.

The proposed model has been proven accurate enough to be of use in the design and development of polymer dispensers for the release of volatile substances. Applications such as insect pheromone and volatile corrosion inhibitor dispensers will benefit from shorter and less costly development cycles. The choice of polymer and dispenser geometry can be narrowed down considerably before it is necessary to manufacture injection-molding tools for release tests. Using the model will allow development of polymer dispensers with fewer tool modifications and smaller release trials.

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