

Prediction of the release characteristics of alcohols from EVA using a model based on Fick's 2nd law of diffusion

by

Arnoldus Jacobus Krüger

A dissertation submitted in partial fulfilment
of the requirements for the degree

Master of Engineering

in the

Faculty of Engineering

University of Pretoria

October 2000

SYNOPSIS

Title: Prediction of the release characteristics of alcohols from EVA using a model based on Fick's 2nd law of diffusion.

Author: Arnoldus Jacobus Krüger

Supervisor: Mr. A.T. Tolmay

Department: CHEMICAL ENGINEERING
UNIVERSITY OF PRETORIA

Degree: Master of Engineering

Volatile substances such as perfumes, insect pheromones and volatile corrosion inhibitors can be released into the atmosphere from polymer matrices. The release characteristics of the volatile substances depend on the original concentration of the substances, and also on the type and geometry of the matrix. The design of the matrix can be done with a trial and error process involving several iterations of tool making followed by testing of the release characteristics. However, this is a costly and time-consuming method.

The objective of this study is to propose and evaluate a mathematical model based on Fick's second law of diffusion. The model can be used to predict the release profiles of volatile substances from polymer matrices based on the initial volatile concentration, matrix geometry and the coefficient of diffusion of the volatile through the polymer. The alcohols 1-propanol, 1-butanol, 1-hexanol and 1-octanol and the polymer ethylene-co-vinyl acetate (EVA) were chosen as a model system for this study.

The coefficients of diffusion of all the alcohols through the EVA were determined with the time lag test using a diffusion cell and polymer sheets. Several methods of making polymer sheets were evaluated. Injection moulded disks was the most suitable method for the system under consideration. Based on the results of the time lag tests, the proposed model was used to predict the release characteristics of the different alcohols from two EVA matrix designs.

Injection moulded test pieces of both designs were prepared. All the test pieces contained ca. 10% of one of the alcohols. The test pieces were aged at ambient conditions and the release of the alcohols was monitored. It was found that the proposed model gave a good prediction of the residual mass of the dispensers, never diverging more than 10% from the experimental result. The experimental results tended to show faster release than predicted. This was expected since the model does not consider the effect of concentration on the coefficient of diffusion.

It was concluded that the model gave accurate predictions of the release characteristics of the system investigated. It would be a useful tool in the design and development of polymer dispensers for volatile substances. The smaller number of tool modifications and release tests required will lead to cost and time savings in the development process.

Keywords: diffusion, diffusion modelling, Fick's 2nd law, controlled release, ethylene-co-vinyl acetate.

SINOPSIS

Titel:	Voorspelling van die vrystellingskaraktersitieke van alkohole uit EVA deur 'n model gebaseer op Fick se 2de wet van diffusie.
Outeur:	Arnoldus Jacobus Krüger
Studieleier:	Mnr. A.T. Tolmay
Departement:	CHEMIESE INGENIEURSWESE UNIVERSITEIT VAN PRETORIA
Graad:	Magister in Ingenieurswese

Vlugtige stowwe soos parfume, insek-feromone en vlugtige korrosie-inhibeerders kan uit polimeermatrikse in die atmosfeer vrygestel word. Die vrystellingsgedrag van die vlugtige stof is afhanklik van die oorspronklike konsentrasie van die stof, die tipe polimeer waarvan die matriks gemaak is en die geometrie van die matriks. The ontwerp van die matriks kan gedoen word deur verskeie iterasies van gietstukmodifikasie en toetsing van die vrystellingsgedrag. Dit is egter 'n duur en tydrowende proses.

Die doel van hierdie studie is om 'n wiskundige model gebaseer op Fick se 2de diffusiewet voor te stel en te evalueer. Die model kan gebruik word om die vrystellingsprofiel van vlugtige stowwe uit polimeermatrikse te voorspel, gebaseer op die beginkonsentrasie, matriksvorm en die diffusiekoëffisient van die vlugtige stof deur die polimeer. Die alkohole, 1-propanol, 1-butanol, 1-heksanol en 1-oktanol asook die polimeer etiel-kovinielasetaat (EVA) is as modelsisteem gekies vir hierdie studie.

Die diffusie koëffisient van al die alkohole deur EVA is bepaal met 'n tydvertragingstoets wat gedoen is met 'n diffusiesel en 'n polimeerfilm. Verskeie metodes om die film te maak is geëvalueer. Spuitgietvorming was die beste metode vir die gekose sisteem. Gebaseer op die resultate van die tydvertragingstoets, is die voorgestelde model gebruik om die vrystellingsprofile van die alkohole uit twee EVA-matriksvorms te voorspel.

Gesputgietvormde toetsstukke is voorberei in die vorm van albei ontwerpe. Al die stukke het ongeveer 10% van een van die alkohole bevat. Die vrystelling van die alkohole is

gemonitor soos wat die stukke verouder het. Daar is gevind dat die model die residuele massas van die matrikse akkuraat voorspel het. Die voorspelling het nooit met meer as 10% van die eksperimentale resultaat afgewyk nie. In alle gevalle was die eksperimentele vrystelling vinniger as wat voorspel is. Dit is te verwagte omdat die model nie die effek van konsentrasie op die diffusie koëffisient in ag neem nie.

Die gevolgtrekking is gemaak dat die model met vrug gebruik kan word in die ontwerp en ontwikkeling van polimeermatrikse vir die vrystelling van vlugtige stowwe. 'n Vermindering in die aantal gietstukmodifikasies en vrystellingstoetse sal koste en tyd bespaar tydens die ontwikkelingsproses.

Sleutelwoorde: diffusie, diffusiemodellering, Fick se 2de wet, beheerde vrystelling, etielko-vinielasetaat.

TABLE OF CONTENTS

Synopsis.....	I
Sinopsis.....	III
Table of contents	V
List of figures & Tables.....	VI
Nomenclature.....	VII
1. Introduction	1
1.1 Background.....	1
1.2 Problem statement	1
1.3 Objective.....	1
1.4 Scope	1
2. Literature and theory	3
2.1 State of the art.....	3
2.1.1 Controlled release of perfumes	3
2.1.2 Controlled release of pheromones	4
2.1.3 Controlled release of volatile corrosion inhibitors	5
2.2 Theory.....	5
2.2.1 Diffusion theory.....	5
2.2.2 Sorption theory	7
2.2.3 Permeation through a polymer film.....	8
2.2.4 Diffusion out of a polymer matrix.....	10
2.3 Literature	13
3. Experimental.....	17
3.1 Materials	17
3.1.1 Polymer.....	17
3.1.2 Solvents	17
3.2 Apparatus.....	17
3.2.1 Mass balance	17
3.2.2 Diffusion cells	17
3.2.3 Micrometer	18
3.2.4 Injection moulder.....	18
3.2.5 Two-roll mill	19
3.2.6 Film blower	19
3.3 Methods	19
3.3.1 Solution casting	19
3.3.2 Time lag tests.....	19
3.3.3 Diffusion modelling.....	20
3.3.4 Release tests.....	20
3.4 Experimental planning.....	21
4. Results & Discussion.....	23
4.1 Time lag tests.....	23
4.2 Diffusion modelling and experimental results	25
4.3 Practical application	29
5. Conclusions	31
6. References	33
Appendix A – Results of time lag tests	A
Appendix B – Results of release tests	B
Appendix C – Results from modelling.....	C

LIST OF FIGURES & TABLES

Figure 2.1: Different types of diffusion behaviour observed in polymer-solvent systems. ...	6
Figure 2.2: Typical curves for sorbed concentrations vs. partial pressure.	7
Figure 2.3: Diagrammatic representation of the cross section of a polymer film.	8
Figure 2.4: Solvent transmission as a function of time	9
Figure 2.5: Schematic representation of an infinite flat plate.....	10
Table 2.1: Summary of relevant literature.....	15
Table 2.1: Summary of relevant literature (continued from page 15).....	16
Figure 3.1: Diffusion cell used for time lag tests	18
Figure 3.2: Diffusion cell with EVA disk.	20
Figure 3.3: Release test pieces.....	21
Figure 3.4: Experimental planning	22
Table 4.1: Time lag test results.....	24
Table 4.2: Residual mass [where ♦ is the experimental result and — is the model]	26
Table 4.3: Release rate [where ♦ is the experimental result and — is the model]	28

NOMENCLATURE

C	Concentration of a solvent in a polymer, g/mm^3
C_0	Concentration of solvent at zero time, g/mm^3
C_s	Concentration of solvent at the surface of a polymer, g/mm^3
D	Coefficient of diffusion, mm^2/h
D_0	D at a reference temperature
E_D	Activation energy of diffusion
EEA	Ethylene-co-ethyl acrylate
EVA	Ethylene-co-vinyl acetate
ℓ	Film thickness, mm
L	Lag time, h
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
M	Mass of polymer dispenser including solvent, g
M_0	Mass at zero time
$N_{x,y,z}$	Solvent flux through polymer at position x,y,z
p	Partial pressure of a solvent in the atmosphere
PET	Polyethyleneterephthalate
PVC	Polyvinyl chloride
Q	Accumulated solvent mass, g
R	Gas constant
S	Henry's constant
t	Time, h
T	Absolute temperature, K
VA	Vinyl acetate
VCI's	Volatile corrosion inhibitors
x	Position on the x-axis of Cartesian coordinates
y	Position on the y-axis of Cartesian coordinates
z	Position on the z-axis of Cartesian coordinates

1. INTRODUCTION

1.1 Background

Polymer matrices are often used to release volatile substances into the atmosphere. Usually these substances only have a beneficial effect if they are present in the atmosphere at certain minimum concentrations. Examples include perfumes, insect pheromones and volatile corrosion inhibitors.

Often these volatile substances are expensive. To have a cost effective release system, the polymer, matrix geometry and volatile content have to be optimised to release the volatile at a rate that is high enough to ensure sufficient concentrations of the volatile in the atmosphere, but low enough to conserve the volatile content of the matrix and ensure the maximum possible lifetime.

1.2 Problem statement

Up to now the polymer type, matrix geometry and volatile loading have been determined mostly by trial and error. This is a costly and time consuming method since it usually requires several iterations of design changes, tool modification and release tests. Since the design is usually aimed at one type of polymer right from the start, it is difficult to compare different polymer matrices without making several sets of tools.

1.3 Objective

The objective of this study is to propose and evaluate a simple method of predicting the release characteristics of volatile substances from polymer matrices by using a mathematical model based on Fick's 2nd law of diffusion.

1.4 Scope

As a model system the alcohols 1-propanol, 1-butanol, 1-hexanol and 1-octanol and the polymer ethylene-co-vinyl acetate (EVA) was chosen. Several methods of making films

from EVA were evaluated. These films were used in time lag tests in order to determine the coefficient of diffusion of the different alcohols through the EVA.

A mathematical model was developed to predict the release characteristics of the alcohols from the EVA. The model was based on Fick's second law of diffusion and had the coefficient of diffusion, volatile concentration and dispenser geometry as inputs. The model predicted the residual mass of a polymer dispenser as a function of time.

Injection moulded matrices of EVA containing 10% of the different alcohols were injection moulded. They were aged at ambient conditions and the release of the alcohols from the matrices was monitored.

The predicted release curves were compared to the experimental results to determine how accurate the model is.

2. LITERATURE AND THEORY

2.1 State of the art

There are many examples where volatile substances are purposely released from polymer matrixes to bring about a beneficial change in the surrounding atmosphere. The volatile substance can be either a good or a poor solvent for the polymer matrix that is used. However, using a poor solvent usually leads to processing problems during the preparation of the dispensers (unpublished research, 1998). For the remainder of this study, volatile substances will be referred to as solvents, although some of the examples mentioned might be of systems where the substance released is in fact not a good solvent for the polymer matrix.

Some applications where the release of solvents from polymer matrixes is of importance will be discussed in this paragraph.

2.1.1 Controlled release of perfumes

Perfumes and volatile fragrances can be released from polymer dispensers to obtain a controlled release profile and therefore longer effective dispenser life (Booma, Hoojjat & Gaicin, 1995; personal communications, 1998). These dispensers are can be used in homes, offices, public places and motorcars.

Two types of dispensers are commonly used. In the first type the fragrance is contained in an impermeable reservoir with a small area consisting of a permeable polymer film through which the fragrance permeates to the outside. In the second type the fragrance is absorbed into the polymer matrix. The polymer matrix is then moulded into the shape of the dispenser. Although the first type has the advantage of a zero order release profile and thus more consistent release rates and a longer life, the second type is much easier to manufacture and usually yields satisfactory performance.

2.1.2 Controlled release of pheromones

Insect pheromones can be used for the detection and monitoring of insect pests, and for the direct control of insect populations (Smith, Baker & Ninomiya, 1983; personal communications and unpublished research, 1997-1999). The first application use insect pheromones to attract insects to traps. Monitoring the number of insects caught in the traps on a daily bases can give an early warning of rising insect populations, and can be used to make decisions on if and when insecticide should be sprayed.

Insect populations can be controlled by a technique called mass trapping, where catching large numbers of insects reduces the insect population and thus the damage they cause to crops. Insect populations can also be controlled by a technique called mating disruption. Here pheromones are released into the atmosphere in high enough concentrations to disrupt communications between male and female insects. Since pheromone trails are hidden by the high concentration of pheromones in the atmosphere, the male and female insects cannot find each other. Thus, mating does not take place and eggs and larvae do not end up in fruit.

Pheromones are expensive because they are either extracted from a magnitude of captured insects, or made by complicated organic synthesis. They are also volatile by nature. In order to make pheromone trapping or mating disruption economically viable, it is necessary to control the rate at which the pheromones are released into the atmosphere. Release from polymer matrices is one effective method of doing this.

Natural rubber (McDonough, 1991) is one of the oldest and most commonly used matrices, especially in trapping lures. Polyvinyl chloride has been investigated (Shailaja & Yaseen, 1995; Shailaja, Ahmed & Yaseen, 1996) for use as release matrix for pheromones. It has the added advantage that release rates can be controlled by varying the plasticiser concentration. Biopolymers such as starch, whey and soy proteins were investigated (Atterholt et al., 1998) but were found to be less effective than paraffin waxes. Some authors (McDonough, 1991) have tried to find empirical models with which to predict pheromone release rates of pheromones from dispensers with specific geometries.

2.1.3 Controlled release of volatile corrosion inhibitors

Volatile corrosion inhibitors (VCI's) are used to prevent corrosion of steel parts during transport and storage. VCI's can be absorbed into wrapping paper, waxes and oils, but due to their volatility they tend to have a limited lifetime.

Imbedding VCI's in polymers prolong their effective lifetime. The polymer matrix can be in the shape of dispensers hanged in storage areas, or even plastic films used to wrap the parts in (unpublished research & personal communications, 1999). Since very low concentrations of VCI's offer corrosion protection, the use of polymer dispensers is a cost effective method of corrosion protection.

2.2 Theory

2.2.1 Diffusion theory

In many polymer-solvent systems, diffusion is governed by Fick's second law. For a three dimensional system described by Cartesian coordinates, Fick's second law can be written as:

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \quad \text{Eq. [2.1]}$$

where C is the concentration of the solvent, t is time and D is the coefficient of diffusion (Comyn, 1985: 3; Welty, Wicks & Wilson, 1984: 514).

D is dependant on temperature (Mears, 1993; Pauly, 1999: VI/544). Variations in temperature affect the activity of the solvent and therefore the rate of diffusion. Over moderate temperature ranges the temperature dependence of the coefficient of diffusion is described by an Arrhenius type equation:

$$D = D_0 e^{\frac{-E_D}{RT}} \quad \text{Eq. [2.2]}$$

Where D_0 is the coefficient of diffusion at a reference temperature, E_D is the activation energy of diffusion, R is the gas constant and T is the absolute temperature. Temperature variations can also affect the coefficient of diffusion by increasing or decreasing polymer chain motion and therefore the free volume of the polymer. If temperature variations cause phase transitions in the polymer (e.g. glass transition or melting of the crystalline phase) there will be drastic changes in the rate of diffusion and a discontinuity in the Arrhenius relationship across the phase transition.

D is also dependant on concentration (Rogers, 1985: 14). High solvent concentrations lead to swelling of the polymer matrix and more free volume. Therefore, D will increase with increasing solvent concentrations. A number of mathematical models that describes the free volume theory have been proposed and were reviewed by Mears (1993).

Many different types of diffusion behaviour have been observed for polymer-solvent systems. It can be summarised in a single diagram with temperature on the one axis and solvent activity on the other.

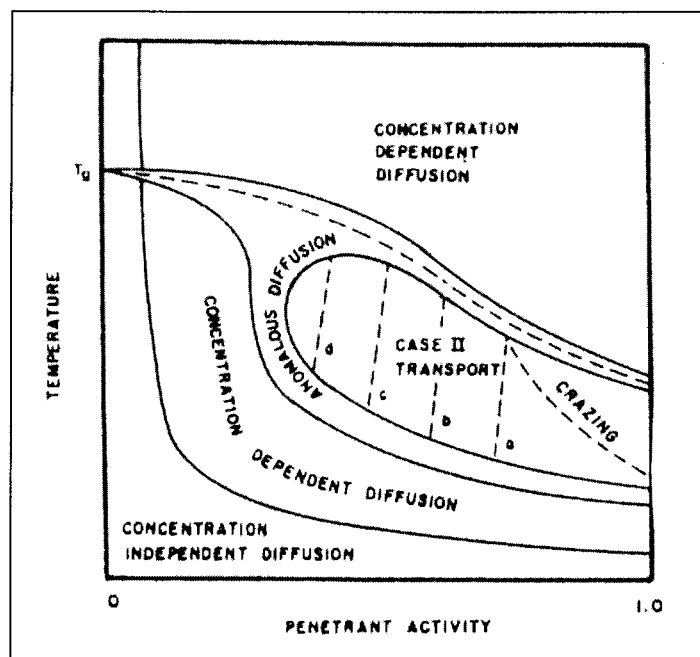


Figure 2.1: Different types of diffusion behaviour observed in polymer-solvent systems (reproduced from Van Krevelen (1990: 576)).

Further discussion of the different types of diffusion behaviour falls outside the scope of this publication. It would suffice to note that for polymers that are at a temperature above

their glass transition, diffusion would be Fickian with D dependant on concentration and temperature.

2.2.2 Sorption theory

Sorption is the process whereby a solvent is adsorbed onto or desorbed from the surface of a polymer. In systems where solvents enter or leave a polymer matrix it is important to keep in mind that different sorption mechanisms exist. Often diffusion is influenced by sorption because it determines the solvent concentrations at the boundaries of the polymer matrix, and thus the concentration gradients that drive the diffusion process.

In most cases it is assumed that Henry's law is valid. For a polymer exposed to an atmosphere containing a solvent vapour with a partial pressure of p , the concentration of solvent at the surface of the polymer, C , will be given by the following equation:

$$C = Sp \quad \text{Eq. [2.3]}$$

Where S is Henry's constant. The following isotherm plots compares Henry's law with other sorption theories.

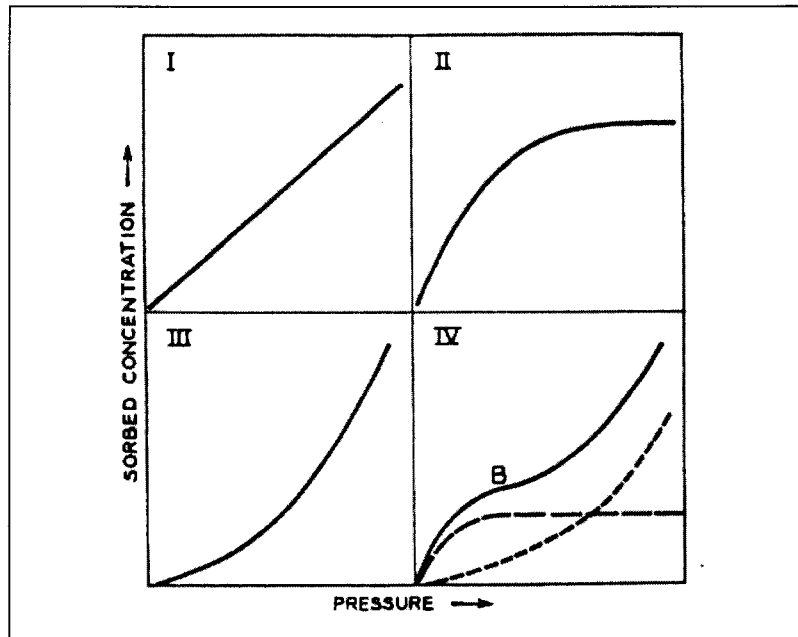


Figure 2.2: Typical curves for sorbed concentrations vs. partial pressure for: I - Henry's law with constant S ; II - Langmuir equation; III - Flory-Huggens equation; IV - BET equation with saturation point B (reproduced from Rogers (1985: 31)).

For the purposes of this study it will be assumed that Henry's law governs sorption. It will also be assumed that sorption will always be a faster process than diffusion. Thus transport kinetics will be governed by diffusion kinetics.

2.2.3 Permeation through a polymer film

Movement of a solvent through a polymer film is called permeation. Permeation consists of three steps (Sweeting, 1968: 596):

- Adsorption of the solvent onto the surface of the membrane
- Diffusion through the membrane
- Desorption or evaporation from the other surface of the membrane

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

Consider a film that is in contact with a solvent containing gas mixture on the one side:

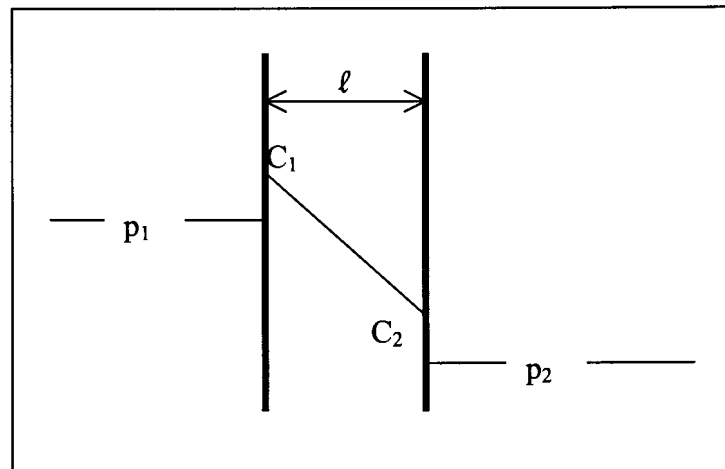


Figure 2.3: Diagrammatic representation of the cross section of a polymer film in contact with a solvent on one side.

Where p_1 and p_2 are the partial pressures of the solvent on the up- and down stream sides of the film respectively, C_1 and C_2 are the concentrations of solvent at the upstream and down stream surfaces of the film and ℓ is the film's thickness.

If it is assumed that:

- Sorption is governed by Henry's law.

- Diffusion is governed by Fick's 2nd law.
- The coefficient of diffusion is independent of concentration.
- The film is initially solvent free.
- Equilibrium is reached at the solvent rich surface.
- The concentration at the solvent poor surface is zero.

It can be shown (Barrer, quoted by Vieth, 1991: 20) that the amount of solvent that moved through the film, Q , is given as a function of time by the equation:

$$Q = \frac{DC_1}{\ell} \left[t - \frac{\ell^2}{6D} \right] - \left[\frac{2\ell C_1}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp \left(\frac{-Dn^2\pi^2 t}{\ell^2} \right) \right] \quad \text{Eq. [2.4]}$$

This equation yields the following curve:

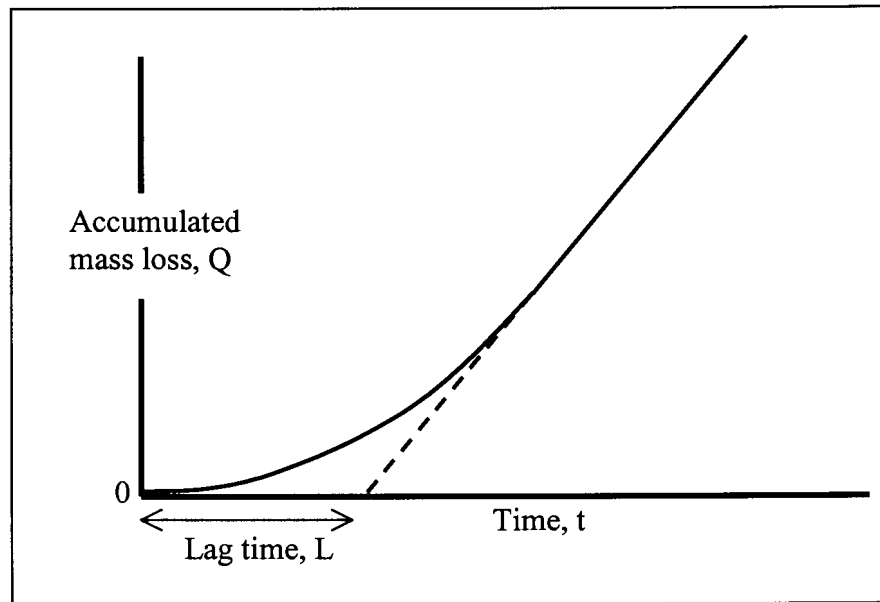


Figure 2.4: Solvent transmission as a function of time

When t becomes large, the second term in equation 2.4 approaches zero. Therefore the linear part of the curve is described by the equation:

$$Q = \frac{DC_1}{\ell} \left[t - \frac{\ell^2}{6D} \right] \quad \text{Eq. [2.5]}$$

If the linear is extrapolated back to $Q = 0$, it follows that $t = L$, which is called the lag time. Substituting into the previous equation it follows that:

$$0 = \frac{DC_1}{\ell} \left[L - \frac{\ell^2}{6D} \right] \quad \text{Eq. [2.6]}$$

Which can be solved to show that:

$$D = \frac{\ell^2}{6L} \quad \text{Eq. [2.7]}$$

This technique is often used to determine the coefficient of diffusion (Rogers, 1985: 21; Sweeting, 1968: 598; Vieth, 1991: 20) and is called the time lag test.

The fact that equation 2.7 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 (Rogers, 1985: 24). However, the time lag test remains a simple and valuable method of determining D and values are often accurate enough for practical purposes.

2.2.4 Diffusion out of 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.

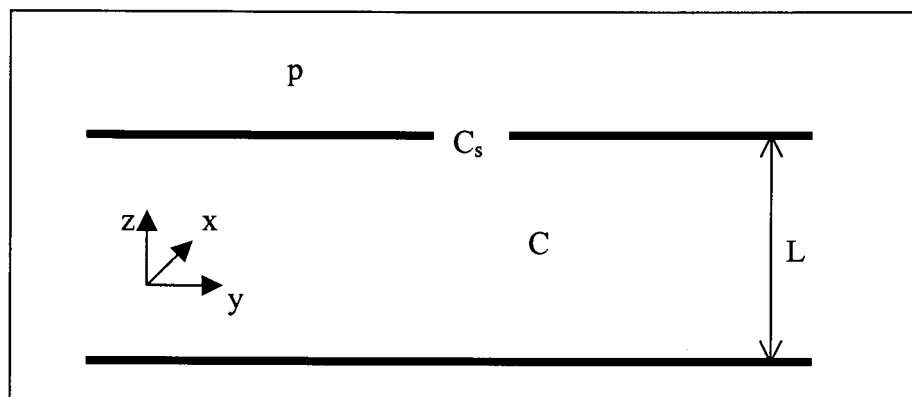


Figure 2.5: Schematic representation of an infinite flat plate.

If it is assumed that:

- Desorption is relatively fast compared to diffusion and governed by Henry's law.
- Fick's law is valid for the polymer-solvent system at the temperature under consideration.
- The temperature and the dimensions of the polymer matrix are constant.
- D is not dependant on C.
- Diffusion in the x and y directions are of no consequence.
- The polymer matrix has a uniform solvent concentration of C_0 at zero time.
- 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 2nd law.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \quad \text{Eq. [2.8]}$$

and the following boundary conditions will be valid:

$$C = C_0 \text{ at } t = 0 \text{ for } 0 \leq z \leq L$$

$$C = C_s \text{ at } z = 0 \text{ for } t > 0$$

$$C = C_s \text{ at } z = L \text{ for } t > 0$$

The solution for this differential equation and boundary conditions is known (Welty, Wicks and Wilson, 1984: 574) to be:

$$N_z = \frac{4D}{L} (C_s - C_0) \sum_{n=1}^{\infty} \left[\cos\left(\frac{\pi n z}{L}\right) \exp\left(\frac{-\pi^2 n^2 t D}{L^2}\right) \right] \quad \text{Eq. [2.9]}$$

where $n = 1, 3, 5, 7, \dots$

and N_z is the solvent flux at the horizontal plain running through z .

Since 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:

$$N_L = -N_0 = \frac{4DC_0}{L} \left[\exp\left(\frac{-\pi^2 tD}{L^2}\right) + \exp\left(\frac{-9\pi^2 tD}{L^2}\right) + \exp\left(\frac{-25\pi^2 tD}{L^2}\right) + \dots \right] \quad \text{Eq. [2.10]}$$

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:

$$\frac{dM}{dt} = -A([N_L] + [N_0]) = -2AN_L \quad \text{Eq. [2.11]}$$

$$dM = -\frac{8ADC_0}{L} \left[\exp\left(\frac{-\pi^2 tD}{L^2}\right) + \exp\left(\frac{-9\pi^2 tD}{L^2}\right) + \exp\left(\frac{-25\pi^2 tD}{L^2}\right) + \dots \right] dt \quad \text{Eq. [2.12]}$$

It is known that:

$$\int \exp(bx) dx = \frac{1}{b} \exp(bx) + k \quad \text{Eq. [2.13]}$$

Thus:

$$\int_{M_0}^M dM = -\int_0^t \frac{8ADC_0}{L} \left[\exp\left(\frac{-\pi^2 tD}{L^2}\right) + \exp\left(\frac{-9\pi^2 tD}{L^2}\right) + \exp\left(\frac{-25\pi^2 tD}{L^2}\right) + \dots \right] dt \quad \text{Eq. [2.14]}$$

Solving this integral equation for M yields:

$$M - M_0 = -\frac{8ADC_0}{L} \left[\left(\frac{-L^2}{\pi^2 D} \right) \left(\exp\left(\frac{-\pi^2 t D}{L^2} \right) - \exp(0) \right) + \left(\frac{-L^2}{9\pi^2 D} \right) \left(\exp\left(\frac{-9\pi^2 t D}{L^2} \right) - \exp(0) \right) + \left(\frac{-L^2}{25\pi^2 D} \right) \left(\exp\left(\frac{-25\pi^2 t D}{L^2} \right) - \exp(0) \right) + \dots \right] \quad \text{Eq. [2.15]}$$

$$M = M_0 - \frac{8ADC_0}{L} \left(\frac{-L^2}{\pi^2 D} \right) \left[\left(\exp\left(\frac{-\pi^2 t D}{L^2} \right) - 1 \right) + \frac{1}{9} \left(\exp\left(\frac{-9\pi^2 t D}{L^2} \right) - 1 \right) + \frac{1}{25} \left(\exp\left(\frac{-25\pi^2 t D}{L^2} \right) - 1 \right) + \dots \right] \quad \text{Eq. [2.16]}$$

$$M = M_0 + \frac{8ALC_0}{\pi^2} \left[\left(\exp\left(\frac{-\pi^2 t D}{L^2} \right) - 1 \right) + \frac{1}{9} \left(\exp\left(\frac{-9\pi^2 t D}{L^2} \right) - 1 \right) + \frac{1}{25} \left(\exp\left(\frac{-25\pi^2 t D}{L^2} \right) - 1 \right) + \dots \right] \quad \text{Eq. [2.17]}$$

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

2.3 Literature

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

Bouzon, Senoune & Vergnaud (1990) and Bouzon & Vergnaud (1991) studied the transport of aniline out of EVA beads immersed in water. 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%.

Mazich, Rossi & Smith (1992) investigated the transport of toluene into cis-1,4-polyisoprene spheres. A model based on Fick's law and taking swelling into account was used to explain the results.

Bakhouya et al. (1992 & 1993) investigated the transport of n-heptane in and out of thin EVA membranes and explained it with a Fickian model that takes swelling and shrinking into account. It was found that the numerical model is more accurate than an analytical model that ignores dimensional changes.

Table 2.1 gives a more thorough comparison of recent publications. The publications in this table deal with the subjects of diffusion modelling and diffusion studies involving EVA. It is by no means an exhaustive list of the available literature on the subject. However, it does give an overview of typical studies in the field under consideration.

Author & year	Objective	Polymer(s)	Solvent(s)	Experimental	Model	Results
Bakhouya et al., 1992	To present a model for liquid absorption by a thin sheet of polymer, taking diffusion and swelling into account Comparison of model with an analytical model	EVA (28% VA)	n-Heptane	Absorption of solvent into polymer sheets gravimetrically monitored	Numerical solution of Fick's law taking swelling into account	Numerical model gives better description of process than analytical model, also more accurate values for D
Bakhouya et al., 1993	To present a model for liquid desorption by a polymer, taking diffusion and swelling into account Comparison of model with an analytical model	EVA (28% VA)	n-Heptane	Sheets were pre-saturated and hung vertically, desorption was monitored gravimetrically	Numerical solution of Fick's law taking shrinkage into account	Numerical solution between experimental data and analytical solution
Booma, Hoojjat & Giacin, 1995	To investigate the effect of air velocity and solvent composition on the permeability of the solvents in the polymer	EVA (5% VA) EEA	Isopar with fragrances	Diffusion through membranes measured in permeation cell with different air velocities over membrane	None	Not possible to predict permeation of mixtures from the data collected for individual components
Bouzon & Vergnaud, 1991	To present a new model for the desorption of liquids from polymers, taking shrinkage into account Comparison of model with an analytical model	EVA (14 – 40% VA)	Aniline	Pre-saturated polymer bead is placed in water, desorption is determined gravimetrically	Numerical solution of Fick's law for sphere, finite element treatment of shrinkage	Model gives good description of desorption Analytical model only accurate for solvent content of less than 10% by volume
Dinh et al., 1992	Investigation of counter diffusion of 2 solvents	EVA (37% VA)	Ethanol Water	Polymer membrane is placed between two solvents, changes in solvent composition is determined by measurement of refractive indices	None	Counter fluxes linearly dependant
Földes, 1994	To study the transport properties of Topanol C in three different ethylene polymers and to determine the relation between D and free volume	LDPE LDPE (60%)+LLDPE (40%) EVA (3% mole)	Topanol CA	Film stack placed in solvent source, concentration in each film determined after a certain time, diffusion coefficient determined from concentration gradient	Free volume theory	Linear relation between ln D and 1/free volume Solubility higher in EVA Solubility depends on exp. Conditions and thermal history
Kumar et al., 1996	To investigate the pervaporation characteristics of Acetone and CCl ₄ through EVA and cross-linked EVA membranes	EVA (18% VA)	Carbon tetrachloride Acetone	EVA crosslinked with DCP and BP and pressed into membranes Pervaporation through membranes tested, upstream solvent in contact with membrane, downstream vacuum	None	Only cross-linked EVA have a selectivity for CCl ₄ , it increase with CCl ₄ content of solvent mixture

Table 2.1: Summary of relevant literature

Kumar, Thomas & Kimaran, 1997	To investigate the effect of peroxide vulcanisation on the sorption and diffusion characteristics of aromatic hydrocarbons through EVA	EVA (18% VA)	Benzene Toluene Xylene	EVA cross-linked with DCP and BP and pressed into samples Absorption of solvent gravimetrically monitored	1 st and second order sorption	Solvent uptake lower for uncross-linked material. Higher for cross-linked material with low cross-link density Diffusion mechanism deviates from Fickian and is anomalous at 28 C, non-Fickian at higher temperatures Transport kinetics are closer to first order than to second order
Mazich, Rossi & Smith, 1992	To propose and test a model for the absorption and desorption of a solvent into and out of a polymer	Cis-1,4-Polyisoprene	Toluene	Rubber spheres were cured with DCP, and immersed in an optical cell containing toluene, swelling was measured from optically. Deswelling was done in both air and methanol.	Model based on Fick's law, taking swelling into account	Correct use of Fick's laws allows model to explain experimental results, both qualitatively and quantitatively
Piergiorganni, Fava & Siciliano, 1995	To present and test a simple model for the prediction of water vapour transmission rate through different polymer films	PET PVC EVA (5% VA) LDPE	Water	Gravimetric and dynamic methods described by ASTM	Water vapour transmission rate dependant on temperature and relative humidity, both influenced by temperature. Arrhenius equation used for temperature dependence of diffusion coefficient, Clausius Clapyron for water vapour pressure.	Model gives good predictions for PET en LDPE, but not for PVC and EVA. Water vapour pressure effect more important than coefficient of diffusion effect.
Senoune, Bouzon & Vergnaud, 1990	To present and test an absorption model	EVA (14, 28 & 40% VA)	Aniline	Polymer beads are soaked in solvent, absorption determined gravimetrically	Based on Fick's law with constant diffusivity, numerical solution with finite element modelling of swelling	Coefficient of diffusion seems to be dependant on degree of swelling, effect is pronounced at high degrees of swelling
Sheppard, Madrid & Langer	To study the swelling and release of BSA from EVA, and to attempt to explain it with a model	EVA (33 & 40% VA)	Bovine serum albumin	Polymer containing BSA disks were placed in buffer solutions, buffer solution were changed at set intervals and analysed to determine BSA content	Qualitative model, considering elastic deformation of polymer caused by swelling of BSA in pores	Release depends on temperature and the elastic modulus of the polymer. The model must be tested mathematically.

Table 2.1: Summary of relevant literature (continued from page 15)

3. EXPERIMENTAL

3.1 Materials

3.1.1 Polymer

Ethylene-vinyl acetate copolymer (EVA) was used as the polymer matrix in this study. EVA is a branched random co-polymer produced by high-pressure radical polymerisation. 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/10min at 190°C and 2.16 kg.

3.1.2 Solvents

The primary alcohols 1-propanol, 1-butanol, 1-hexanol and 1-octanol were used as solvents in this study. All solvents were obtained from Saarchem, except for the 1-hexanol, which was obtained from Merck. All solvents were CP grade; except for 1-butanol which was AR grade.

3.2 Apparatus

3.2.1 Mass balance

The samples were weighed on a calibrated Satorius Research balance with an accuracy of 0.1 mg.

3.2.2 Diffusion cells

The diffusion cells used in this study were machined from aluminium and had the following design:



Figure 3.1: Diffusion cell used for time lag tests

The cells consisted of an aluminium base cup, a rubber O-ring, aluminium sealing ring and an aluminium top. The O-ring fits on top of the base cup. The polymer film 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 film 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 film.

3.2.3 Micrometer

The thickness of the EVA films and disks were measured with a Mitutoyo digital micrometer with an accuracy of 1 micron.

3.2.4 Injection moulder

An Engel 3020 injection moulding machine with an 800 kN clamping unit was used to mould the time lag as well as the release test pieces. It has 4 temperature zones which were set to 60, 70, 80 and 90°C respectively. Moulding pressure of ca. 12bar was used and the samples were cooled for 25 seconds in a mould with a temperature of ca. 25°C.

3.2.5 Two-roll mill

A two-roll mill built by David Bridge & Co. Ltd was used to manufacture calendared films. The rolls were heated to 60°C by circulating heating oil through them. The EVA granules were rolled through a roller gap of 1mm until they fused, where after the roller gap was adjusted down to the required thickness of the films being made.

3.2.6 Film blower

A custom-built film blower with a ring-die with a diameter of 25mm and a blow-up ratio of 4 was used to produce blown films. Processing temperatures were 60, 70 and 80°C at the feeding zone, barrel and die respectively.

3.3 Methods

3.3.1 Solution casting

Solution cast films were made in the following manner. A 20% by mass solution of EVA in technical toluene was prepared. It was poured into a petri-dish so that the bottom was covered with ca. 1mm of the solution. The petri-dish was then placed in an laboratory oven set to a temperature of 50°C and left to stand overnight. The films were removed and placed on a grid in a well-ventilated laboratory for a week before they were used in the time lag tests.

3.3.2 Time lag tests

Approximately 20 ml of solvent was placed in each of the diffusion cells. An injection moulded 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°C ±2°C. However, the area was well ventilated to prevent a build up of solvent in the atmosphere. The cells were weighed at regular intervals. The coefficient of diffusion was determined using the method described in par.2.2.3. Data was plotted in the shape of figure 2.4, the lag time was determined graphically and equation 2.7 was used to calculate the value of D.

Figure 3.2 shows a diffusion cell containing an injection-moulded EVA disk.



Figure 3.2: Diffusion cell with EVA disk.

3.3.3 Diffusion modelling

The diffusion model was based on the equation 2.17. The residual mass of the release test pieces were estimated with the equation:

$$M = M_0 + \frac{8ALC_0}{\pi^2} \left[\left(\exp\left(\frac{-\pi^2 tD}{L^2}\right) - 1 \right) + \frac{1}{9} \left(\exp\left(\frac{-9\pi^2 tD}{L^2}\right) - 1 \right) + \frac{1}{25} \left(\exp\left(\frac{-25\pi^2 tD}{L^2}\right) - 1 \right) + \dots \right] \quad \text{Eq. [3.1]}$$

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 2 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.

3.3.4 Release tests

EVA granules were mixed with approximately 10% by mass of a solvent. The mixture was sealed in a glass jar with a rubber seal and left to stand at room temperature until the polymer had absorbed most of the solvent.

The mixture was then injection moulded into two types of 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 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 moulding the disks were sealed in glass jars and left to stand overnight at 23°C. After ca. 24 hours the disks were removed from the jars and placed on a steel grid in the temperature controlled laboratory. They were weighed immediately and thereafter at regular intervals. Weighing was continued until the rate of mass loss approached zero.

Figure 3.3 shows some release test pieces on a steel grid.

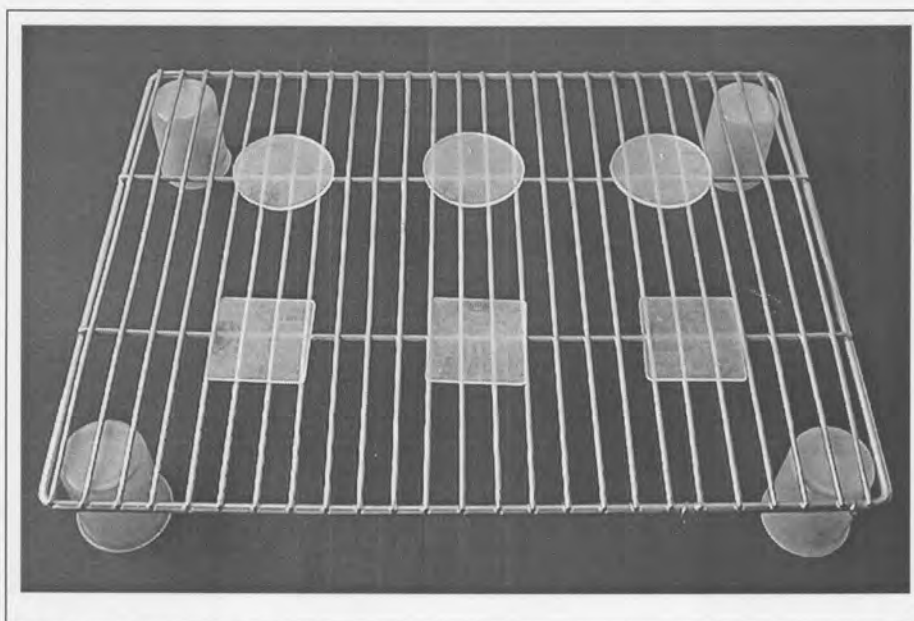


Figure 3.3: Release test pieces.

3.4 Experimental planning

The EVA/alcohol system was selected for several reasons. Most insect pheromones are either alcohols or acetates, and therefore it was felt that the chosen system would give a good indication of whether the model would be suitable for the release of pheromones from EVA. EVA was chosen because of its compatibility with alcohols and its low processing temperature ($<100^{\circ}\text{C}$), which allows it to be shaped into dispensers without a

significant loss of solvent. Four alcohols were used to verify the model over a range of volatilities.

The geometries of the release samples were determined by the injection moulding tools available for this study. Flat shapes with varying thickness were chosen to verify the model for different thickness. Both samples had relatively large top and bottom surface areas compared to the side areas. This simplified the modelling because side areas could be ignored.

Thus, one type of polymer, four alcohols and two geometries were evaluated. Therefore, four time lag tests had to be done to determine the coefficient of diffusion for each alcohol. Each alcohol was incorporated into two geometries for the release tests, yielding eight results for the release tests. Each case was also modelled based on the results of the time lag tests. Therefore, eight predicted curves could be compared to eight experimental curves to verify the model. A scheme for the experimental planning is shown in figure 3.2.

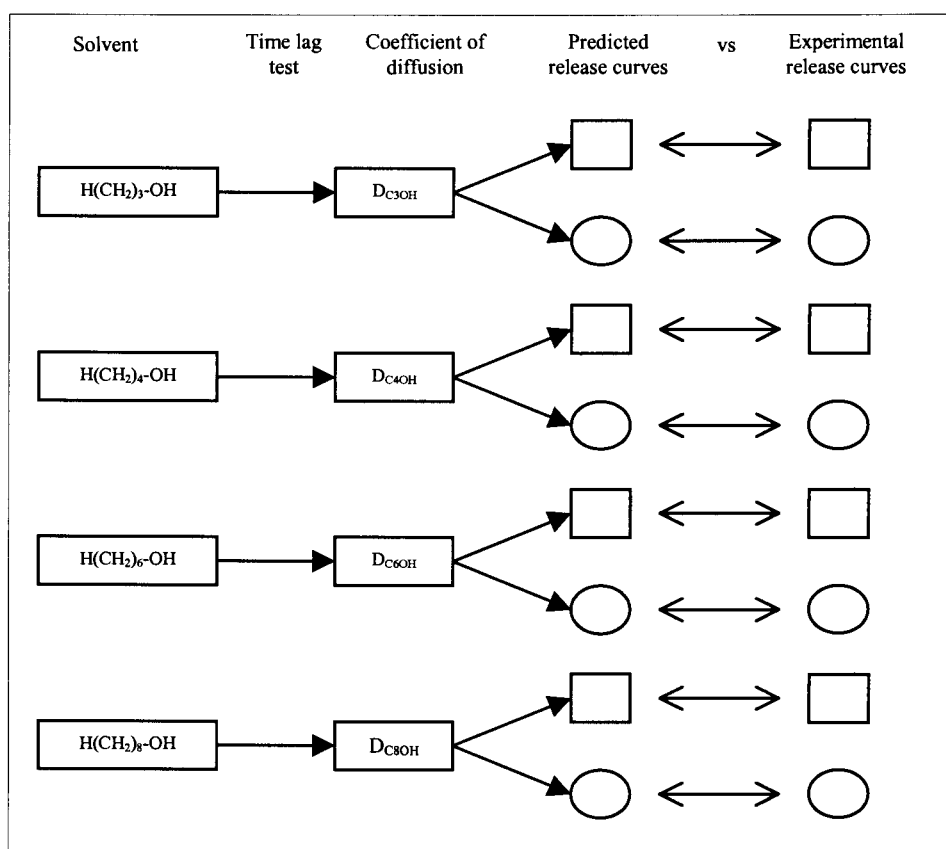


Figure 3.4: Experimental planning

4. RESULTS & DISCUSSION

4.1 Time lag tests

Film or sheets for use in time lag tests can be made in various ways. In this study films were produced by solution casting, film blowing and calendaring. Solution casting and film blowing worked well but the films produced in this manner showed significant (up to 20%) variation in thickness, which will cause inaccuracy in the results of the time lag tests. With solution-cast films, there is the added problem that the coefficient of diffusion might be affected if all the solvent used for casting is not removed during the drying stage. Calendered films were uniform in thickness, but the calendaring process tended to yield warped films. The calendered films also had a tendency to form surface blisters and other irregularities which rendered them useless for time lag tests.

For this reason injection moulded disks with a thickness of ca. 3mm was used for the time lag tests. Because of the thickness of the disks, permeation was slow which made it easier to calculate the coefficient of diffusion accurately. A major drawback of the thicker disks is that the time lag tests takes much longer to run to completion than with thinner films. Film extrusion with a flat film die will probably be the best option. Films will be thicker than blown films and there will be better control over film thickness. However, the equipment required was not available for use in this study.

The time lag tests were run for between 1000 and 1200 hours each (6-7 weeks). The data was plotted in the form of figure 2.4, lag time was determined graphically and the coefficient of diffusion, D , was calculated using equation 2.7. Unfortunately, several samples were found to have leaking diffusion cells, which meant that the results had to be calculated from a relatively small number of samples. The following results were obtained for the four solvents:

Solvent	Number of samples	Average coefficient of diffusion, 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

Table 4.1: Time lag test results

Another problem that was encountered was that the linear part of the time lag test curve showed a slight increase in slope as the test progressed. Because alcohols are good solvents for EVA, the disks tended to swell which caused an increase in free volume and, therefore, in the rate of diffusion. This meant that the lag times observed were longer if the last part of the curve was extrapolated back to the x-axis. Since longer lag times yields lower diffusion coefficients, the results of the time lag tests become more inaccurate with time. For this reason the coefficient of diffusion was calculated by extrapolating the earliest linear part of the permeation curve. Because of the non-linearity, lag times were calculated by hand using a graphical method. Lag times were read off to the nearest 5 hours. For linear lines a straight-line regression can be done. The intersection of the regression with the x-axis can be calculated to obtain a more accurate lag time.

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, solventless control samples 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.

4.2 Diffusion modelling and experimental results

The diffusion model and the results from the release tests were compared in two ways. The residual mass vs. time curve was plotted against the predicted curve. This represents the direct result obtained from the model. Using this data the rate of release was calculated for both the experimental results and the prediction. This is done because in many applications the release rate is the most important factor.

The following results were obtained for the eight samples under consideration. The experimental curves are the average of three samples each.

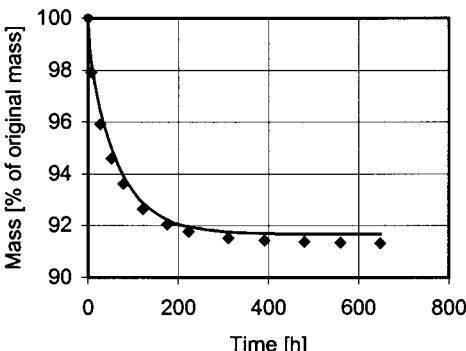
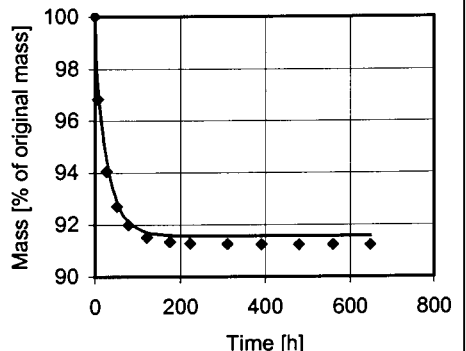
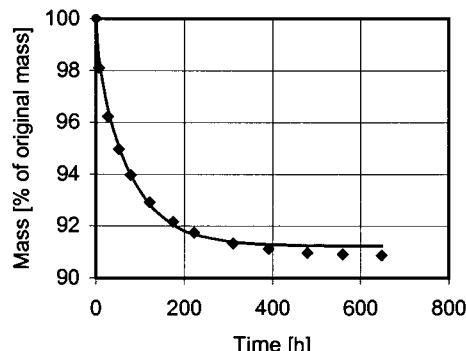
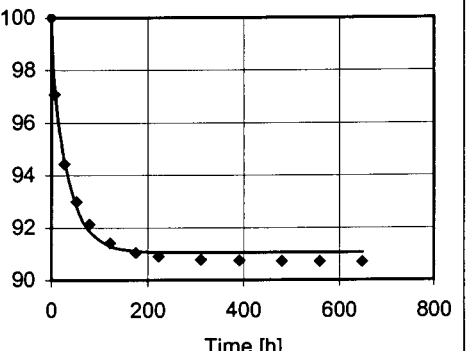
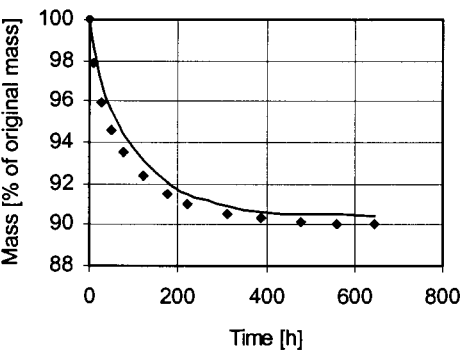
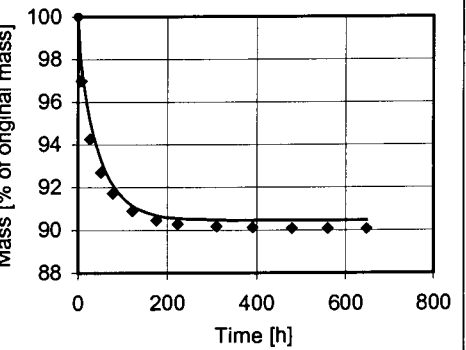
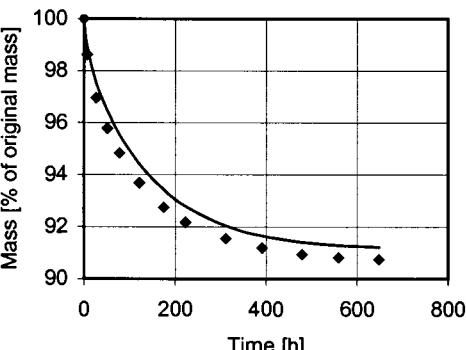
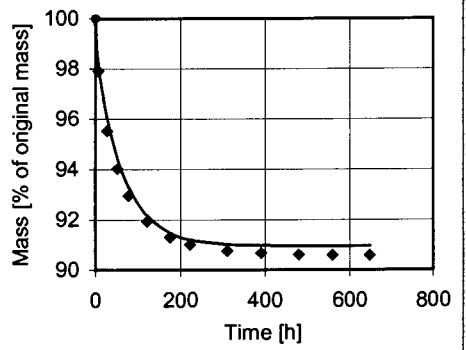
	Round samples	Square samples
1-Propanol		
1-Butanol		
1-Hexanol		
1-Octanol		

Table 4.2: Residual mass [where \blacklozenge is the experimental result and — is the model]

The models gave good predictions of residual mass in all cases. It never diverged more than 1% from the experimental result. Since 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 since the model used does not consider swelling. It has been shown (Bakhouya et al., 1992 & 1993; Bouzon & Vergnaud, 1991; Senoune, Bouzon & Vergnaud, 1990) 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 rather than an inherent flaw in 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 due to the fact that the square disks are thinner. 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.

The release rates were predicted more accurately than the residual mass. The release rate is equal to the slope of the residual mass. Therefore, the release rate curves will match even if the modelled residual mass curve is slightly higher or lower than the experimental curve. Since release rate is the most important factor in many applications, (e.g. insect pheromones), the model is very useful in this respect. The effective lifetime (the time taken to reach a minimum specified release rate) of a polymer dispenser can be predicted accurately using this model.

The following results were obtained for the eight samples when the release rate was calculated from the residual mass result. The experimental curves are the average of three samples each.

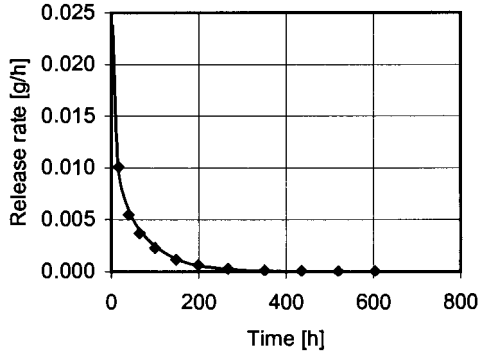
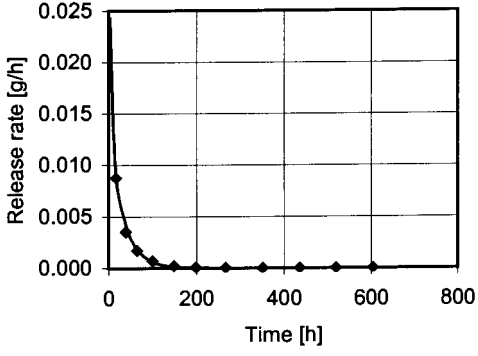
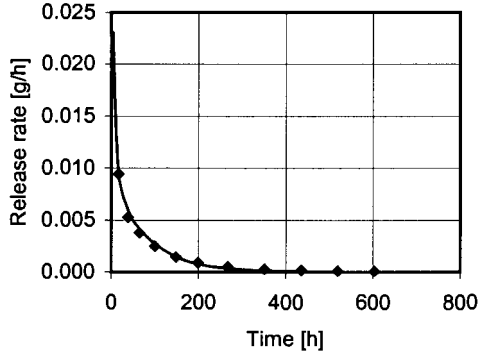
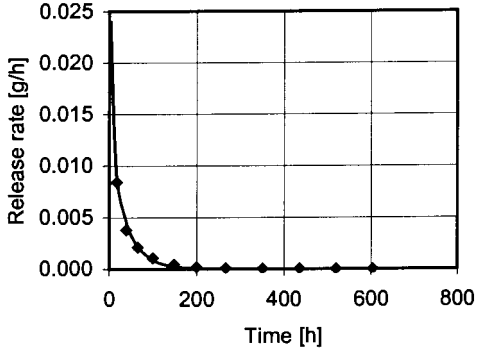
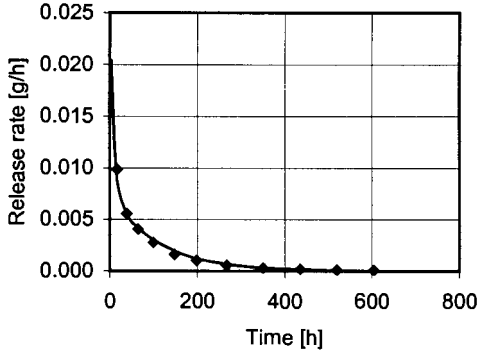
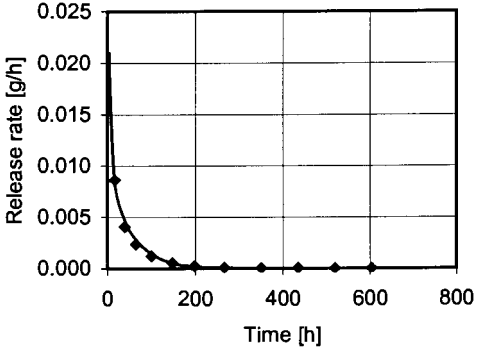
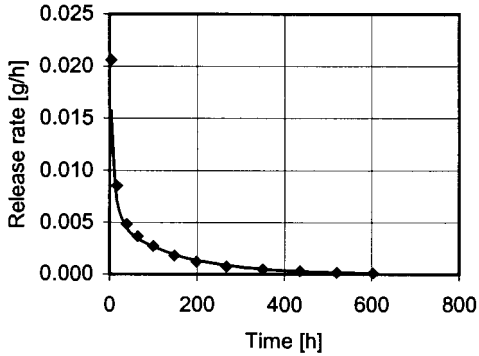
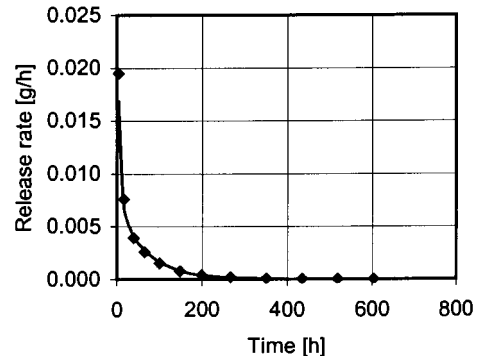
	Round samples	Square samples
1-Propanol		
1-Butanol		
1-Hexanol		
1-Octanol		

Table 4.3: Release rate [where \blacklozenge is the experimental result and — is the model]

4.3 Practical application

Based on the results, the following algorithm is proposed for the development of a polymer dispenser for the release of insect pheromones (which are typically alcohols and acetates containing 9 to 16 carbon atoms).

Step 1 - Specification

- Specify the type of pheromone to be used.
- Specify minimum effective release rate required (mass per area per time).
- Specify dispenser density (number of dispensers per area).
- Calculate minimum required release rate per dispenser.
- Specify minimum lifetime expected of dispenser (time).
- Obtain meteorological data; especially time averaged temperatures and relative humidities.

Step 2 – Polymer selection

- Determine the boiling point of the pheromone.
- List thermoplastic polymers according to lowest possible processing temperature. Discard all polymers which cannot be processed at temperatures at least 10°C lower than the boiling point of the pheromone.
- Mark polymers as semi-crystalline or amorphous.
- Obtain solubility parameters for all polymers as well as the pheromone.
- Select best candidates. Preference must be given to those polymers which are amorphous and which has a solubility parameter close to that of the pheromone. In practice the choice is usually quite limited, especially for the lower boiling pheromones. Figure 2.1 should be kept in mind. Polymers that are above their glass transition at operating temperature are probably a better choice.
- Select commercially available grades based on availability, price and other factors (e.g. biodegradability).

Step 3 - Time lag tests

- Prepare 0.2 - 0.5mm thick films from best candidates using flat film extrusion (or alternatively use injection moulded disks).
- Do the time lag tests in a temperature and humidity controlled laboratory set to the time averaged temperature and humidity specified in step 1.

- Calculate the coefficient of diffusion of the pheromone for each of the polymers.

Step 4 – Design and modelling

- Assume a simple (round or square) flat shape with a thickness of 2 – 4mm.
- Assume a pheromone concentration of 5 – 10% of the dispenser mass.
- Predict the expected mass vs. time characteristic for the dispenser.
- Compare with the release rate and lifetime specification.
- Adjust dispenser design and thickness until the specification can be met with the lowest possible pheromone concentration.
- Change design to incorporate other features such as integral clips and corporate logos.

Step 5 – Verification

- Manufacture an injection-moulding tool according to the design.
- Prepare dispensers with the specified pheromone concentration.
- Do release tests under controlled conditions.
- If the dispensers do not meet the specifications, slight changes to the dispenser design and pheromone concentration can be made to rectify this.
- Do field tests, i.e. place dispensers under actual conditions and monitor the release of pheromone into the atmosphere. The effectiveness of the dispensers can be determined by monitoring insect activity and comparing it other areas.

Although this algorithm seems quite long, it should lead to cost and time savings during design and development. Trial and error methods rely on the laboratory testing (and sometimes field-testing) of a wide range of polymer types and pheromone concentrations. If specifications are still not met after several iterations changes to the design of the tool is made and the process is repeated.

Tool making, tool modification and field-testing are the most costly and time consuming steps in the development process. Using the proposed model can greatly reduce the number of times that these steps have to be repeated. This can lead to significant savings in cost and time.

5. CONCLUSIONS

Problems were encountered with the preparation of films by solution casting, film blowing and calendaring. Eventually injection moulded disks were used for time lag tests. Although this worked well, the tests had to be run for long times which limited the number of experiments possible in this study. For this reason standard deviations were relatively high.

Water absorption accounted for less than 1% of the total mass variation, both in time lag tests and in release experiments. This means that for the EVA/alcohol systems humidity controlled laboratories are not required.

The proposed model predicted the residual mass to within 10% of the actual value. Good predictions of the release rate from the polymer matrices were obtained. The experimental release tests showed a slightly higher release rate than predicted in most cases. This was expected since the assumption that the coefficient of diffusion is independent of concentration was known to be wrong from the literature. 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 type and dispenser geometry can be narrowed down considerably before it is necessary to manufacture injection-moulding tools for release tests. Using the model will allow development of polymer dispensers with fewer tool modifications and smaller release trials.

Certain modifications to the experimental method used in this study are proposed. The use of extruded films with thickness of 0.2 – 0.5mm will shorten the time required to obtain the results from the time lag tests. The design of diffusion cells is also an important consideration. Diffusion cells which can be closed with flange clamps rather than screw thread will reduce the frequency at which leaking samples are encountered. Although it has been proven that water absorption does not have a major influence on the results, a humidity-controlled laboratory will improve accuracy.

Temperature variations can also lead to inaccuracy. Temperature variations do occur under actual conditions of use. It is recommended that the time-weighted average values of D at different temperatures be used if a high degree of temperature variation is experienced. Determination of D at the time-weighted average temperature is not sufficient because there is an Arrhenius relationship between D and temperature.

There are some applications where the model cannot be used. This includes systems where solvent mixtures are used, e.g. perfumes in a volatile carrier. Systems where the solvent is prone to oxidation, e.g. some types of insect pheromones, will also require analytical verification since the concentration of active solvent might be lower than the total solvent concentration predicted by the model. Outdoor applications such as pheromones might also be affected by factors such as wind speed that will be difficult to incorporate into the model.

6. REFERENCES

- Atterholt, C.A., Delwiche, M.J., Rice, R.E. and Krochta, J.M. (1998) "Study of Biopolymers and Paraffin as Potential Controlled-Release Carriers for Insect Pheromones" *Journal of Agricultural and Food Chemistry*, 46, 4429-4434.
- Bakhouya, A., El Brouzi, A., Bouzon, J. and Vergnaud, J.M. (1992) "Process of absorption of a liquid by a thin sheet of polymer by considering diffusion and change in dimension" *European Polymer Journal*, 28 (7), 809-815.
- Bakhouya, A., El Brouzi, A., Bouzon, J. and Vergnaud, J.M. (1993) "Modelling the process of desorption of a liquid from a sheet of polymer by considering the diffusion and evaporation and the change in dimension" *Plastics, Rubber and Composites Processing and Applications* 19, 77-86.
- Booma, M., Hoojjat, P. and Gaicin, J.R. (1995) "Methodology for evaluating the transmission profile of fragrance volatiles through a semi-permeable delivery system" *Journal of Plastic Film & Sheeting*, 11, 58-78.
- Bouzon, J. and Vergnaud, J.M. (1991) "Modelling of the process of desorption of liquid by polymer beads, by considering diffusion and shrinkage" *European Polymer Journal*, 27 (2), 115-120.
- Comyn J. (1985) "Introduction to Polymer Permeability and the Mathematics of Diffusion" in *Polymer permeability*, J. Comyn (Ed.), Elsevier Applied Science, London, 1-10.
- Dinh, S.M., Berner, B., Sun, Y. and Lee, P.I. (1992) "Sorption and transport of ethanol and water in poly(ethylene-co-vinyl acetate) membranes" *Journal of Membrane Science*, 69, 223-234.
- Földes, E. (1994) "Transport of small molecules in polyolefins. III. Diffusion of Topanol CA in ethylene polymers" *Journal of Applied Polymer Science*, 51, 1581-1589.

- Kumar, S.A., Gedam, P.H., Kishan Prasad, V.S., Kumaran, M.G. and Thomas, S. (1996) "Pervaporation of chlorinated hydrocarbon-acetone mixtures through poly(ethylene-co-vinyl acetate) membranes" *Journal of Applied Polymer Science*, 60, 735-741.
- Kumar, S.A., Thomas, S. and Kumaran, M.G. (1997) "Transport of aromatic hydrocarbons through poly(ethylene-co-vinyl acetate) membranes" *Polymer*, 38 (18), 4629-4640.
- Mazich, K.A., Rossi, G. and Smith C.A. (1992) "Kinetics of solvent diffusion and swelling in a model elastomeric system" *Macromolecules*, 25, 6929-6933.
- McDonough, L.M. (1991) "Controlled Release of Insect Pheromones from a Natural Rubber Substrate" *ACS Symposium Series 449: Naturally Occurring Pest Bioregulators*, P.A. Hedin (Ed.), American Chemical Society, Washington DC, 106-123.
- Mears P. (1993) "The influence of penetrant concentration on the diffusion and permeation of small molecules in polymers above T_g " *European Polymer Journal*, 29, 237-243.
- Pauly S. (1999) "Permeability and Diffusion Data" in *Polymer Handbook*, J. Brandrup, E.H. Immergut and E.A. Grulke (Eds.), John Wiley & Sons Inc., New York, VI 543-571.
- Piergiovanni, L., Fava, P. and Siciliano, A. (1995) "A mathematical model for the prediction of water vapour transmission rate at different temperature and relative humidity combinations" *Packaging Technology and Science*, 8, 73-83.
- Rogers, C.E. (1988) "Permeation of gases and vapours in polymers" *Polymer permeability*, J. Comyn (Ed.), Elsevier Applied Science, London, 11-74.
- Senoune, Bouzon, J. and Vergnaud, J.M. (1990) "Modelling the process of liquid absorption by a polymer sphere, by consideration of diffusion and subsequent swelling" *Journal of Polymer Engineering*, 9 (3), 213-236.
- Shailaja, D. and Yaseen, M. (1995) "Eco-Friendly polymer dispensers for controlled release of agrochemicals" *Proceedings RC IEEE-EBMS & 14th BMESI*, Publisher unknown.

Shailaja, D., Ahmed, S.M. and Yaseen, M. (1997) "Comparative study of release kinetics of pheromone from polymer dispensers" *Journal of Applied Polymer Science*, 64, 1373-1380.

Sheppard, N.F., Madrid, M.Y. and Langer, R. (1992) "Polymer matrix controlled release systems: influence of polymer carrier and temperature on water uptake and protein release" *Journal of Applied Polymer Science*, 46, 19-26.

Smith, K.L., Baker, R.W. and Ninomiya, Y. (1983) "Development of Biolure controlled release pheromone products" in *Controlled Release Delivery Systems*, T.J. Roseman and S.Z. Mansdorf (Eds.), Marcel Dekker Inc., New York, 325-335.

Sweeting, O.J. (1968) *The Science and Technology of Polymer Films*, Interscience Publishers, New York.

Van Krevelen, D.W. (1990) *Properties of Polymers*, Elsevier, Amsterdam.

Vieth, W.R. (1991) *Diffusion in and Through Polymer: Principles and Applications*, Hanser Verlag, München.

Welty, J.R., Wicks, C.E. and Wilson, R.E. (1984) *Fundamentals of momentum, heat and mass transfer*, John Wiley & Sons Inc., New York.

APPENDIX A – RESULTS OF TIME LAG TESTS

Explanatory note – Time lag tests

Seven time lag experiments were done in total. Experiments 1 and 2 were done with blown and solution cast films. No results could be obtained from these because the films were too thin. Experiment 3 was done with injection-moulded disks in a drawing cupboard. The flow of air across the samples caused too much variation in the rate of permeation. Experiment 4 was done similar to 3, except that it was done on an open shelf out of direct air movement. However, the temperature was not controlled at all times and temperatures as high as 30° were recorded. Therefore, the result of experiment 4 was also ignored. Experiments 5, 6 and 7 were done like experiment 4, the only difference being that they were done at 23°C ±2°C.

Three types of behaviour were observed in the results of the time lag tests.

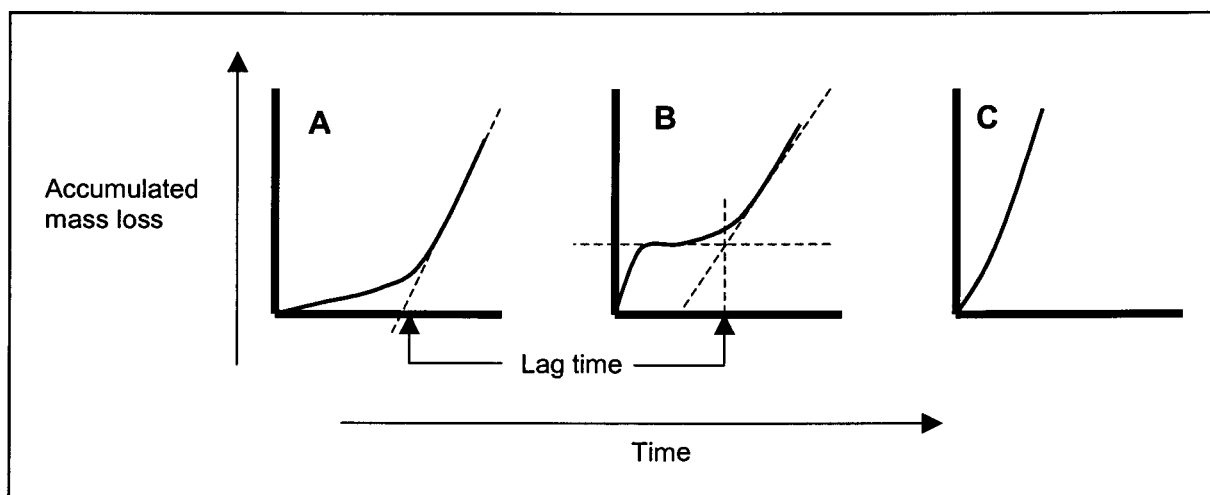


Figure A1: Behaviour of time lag tests

Type A is the expected behaviour. The lag time could be determined by extrapolating the linear part of the curve to the baseline. A slight increase in slope due to swelling of the films was noted. For this reason the earliest linear part of the curve was extrapolated. The ranges used are given in the summary of the results.

Type B behaviour is caused by O-rings that leak until they are swollen by the solvent. Type B results were usually identical to type A results, the only exception being that the baseline was shifted upwards by the amount of solvent that leaked out at the beginning of the test. In these cases a second construction was done at the real baseline in order to determine the lag time.

Type C behaviour is probably caused by leaking diffusion cells and these samples were ignored.

This appendix contains a summary of the results from experiments 5-7, raw data for experiments 5-7 and copies of all graphs with hand drawn construction lines.

Summary of the results of experiments 5,6 and 7

Sample No.	Thickness mm	Lag time h	D mm ² /h	Linear range h	Average mm ² /h	Sdt Dev mm ² /h	Std Dev %
Propanol				200 - 400	1.322E-02	5.49E-04	4.2
6A1	2.986	105	14.2E-3				
6A2	2.955	110	13.2E-3				
6A3	2.913	110	12.9E-3				
7A1	2.971	115	12.8E-3				
7A2	2.962						
7A3	3.004	115	13.1E-3				
Butanol				300 - 500	1.154E-02	8.16E-04	7.1
5A1	3.011	115	13.1E-3				
5A2	3.003	130	11.6E-3				
5A3	3.032	135	11.3E-3				
6B1	3.050	135	11.5E-3				
6B2	2.960	145	10.1E-3				
6B3	2.919	130	10.9E-3				
7B1	2.980	125	11.8E-3				
7B2	2.976	125	11.8E-3				
7B3	3.024	130	11.7E-3				
Hexanol				400 - 600	8.22E-03	3.01E-04	3.7
5B1	3.008	190	7.9E-3				
5B2	3.048	185	8.4E-3				
5B3	3.009	180	8.4E-3				
6C1	2.966	170	8.6E-3				
6C2	2.945						
6C3	2.986	180	8.3E-3				
7C1	3.006	195	7.7E-3				
7C2	2.975	175	8.4E-3				
7C3	2.980	185	8.0E-3				
Octanol				500 - 700	6.16E-03	4.05E-04	6.6
5C1	3.125	240	6.8E-3				
5C2	3.022	260	5.9E-3				
5C3	3.125						
6D1	3.006	240	6.3E-3				
6D2	2.939	250	5.8E-3				
6D3	2.917						
7D1	3.032	250	6.1E-3				
7D2	3.046						
7D3	3.004						

Experiment 5 - Raw data

Alcohol				1-Butanol	1-Butanol	1-Butanol	1-Hexanol	1-Hexanol	1-Hexanol	1-Octanol	1-Octanol	1-Octanol	None	None	None
Film thickness		mm		3.011	3.003	3.032	3.008	3.048	3.009	3.125	3.022	3.125	3.046	3.017	3.023
Mass of diffusion cell (g)															
Date	Day	Hour	Time	A1	A2	A3	B1	B2	B3	C1	C2	C3	D1	D2	D3
25.01.2000	0	15.50	0	167.9303	165.5795	169.4336	167.9623	168.5034	167.9517	168.6977	168.9336	159.0475	145.8488	146.1274	146.1567
	0	17.00	2	167.9282	165.5774	169.4333	167.9621	168.5034	167.9516	168.6980	168.9337	159.0472	145.8487	146.1273	146.1566
	1	7.75	16	167.9232	165.5724	169.4323	167.9625	168.5045	167.9526	168.6988	168.9347	159.0248	145.8498	146.1282	146.1574
	1	16.80	25	167.9203	165.5707	169.4318	167.9626	168.5049	167.9528	168.6994	168.9354	159.0062	145.8484	146.1282	146.1574
	2	16.33	49	167.9162	165.5675	169.4334	167.9655	168.5083	167.9558	168.7029	168.9392	158.9540	145.8520	146.1306	146.1597
28.01.2000	3	16.40	73	167.9103	165.5619	169.4316	167.9666	168.5096	167.9566	168.7048	168.9413	158.9123	145.8514	146.1300	146.1592
31.01.2000	6	8.50	137	167.8547	165.5105	169.3875	167.9493	168.4894	167.9384	168.6994	168.9345	158.7839	145.8451	146.1239	146.1530
01.02.2000	7	10.75	163	167.8238	165.4822	169.3608	167.9372	168.4730	167.9244	168.6978	168.9320	158.7642	145.8487	146.1269	146.1561
	8	14.40	191	167.7824	165.4450	169.3245	167.9169	168.4466	167.9015	168.6900	168.9217	158.7407	145.8465	146.1251	146.1544
04.02.2000	10	13.75	238	167.7016	165.3726	169.2527	167.8710	168.3893	167.8518	168.6679	168.8953	158.6954	145.8464	146.1251	146.1542
07.02.2000	13	13.60	310	167.5773	165.2615	169.1390	167.7825	168.2862	167.7607	168.6216	168.8427	158.6302	145.8497	146.1280	146.1573
	15	11.40	356	167.5030	165.1946	169.0707	167.7250	168.2206	167.7030	168.5884	168.8062	158.5893	145.8517	146.1300	146.1594
	17	14.00	407	167.4222	165.1211	168.9952	167.6640	168.1505	167.6416	168.5498	168.7653	158.5431	145.8533	146.1317	146.1610
	20	12.40	477	167.2957	165.0052	168.8760	167.5702	168.0430	167.5478	168.4885	168.6992	158.4694	145.8546	146.1329	146.1622
17.02.2000	23	10.60	547	167.1561	164.8777	168.7446	167.4665	167.9260	167.4443	168.4183	168.6212	158.3819	145.8505	146.1292	146.1586
22.02.2000	28	9.60	666	166.9239	164.6667	168.5282	167.2947	167.7379	167.2743	168.3092	168.4983	158.2386	145.8506	146.1289	146.1580
25.02.2000	31	14.75	743	166.7771	164.5327	168.3906	167.1840	167.6167	167.1609	168.2378	168.4173	158.1451	145.8517	146.1301	146.1593
01.03.2000	36	11.75	860	166.5354	164.3126	168.1631	166.9999	167.4230	166.9733	168.1201	168.2878	157.9878	145.8505	146.1289	146.1580
06.03.2000	41	15.67	984	166.2823	164.0859	167.9246	166.8090	167.2204	166.7745	167.9958	168.1656	157.8259	145.8511	146.1296	146.1589
14.03.2000	49	10.00	1171	165.9098	163.7525	167.5712	166.5245	166.9106	166.4736	167.8015	167.9818	157.5832	145.8509	146.1293	146.1588

Experiment 6 - Raw data

Alcohol				1-Propanol	1-Propanol	1-Propanol	1-Butanol	1-Butanol	1-Butanol	1-Hexanol	1-Hexanol	1-Hexanol	1-Octanol	1-Octanol	1-Octanol
Film thickness		mm		2.986	2.955	2.913	3.050	2.960	2.919	2.966	2.945	2.986	3.006	2.939	2.917
Mass (g)															
Date	Day	Hour	Time	A1	A2	A3	B1	B2	B3	C1	C2	C3	D1	D2	D3
31.07.2000	0	11.50	0	174.9415	175.3120	175.2877	175.7817	174.8075	170.9541	176.1898	176.6034	175.9975	172.7042	172.8057	171.4481
	0	17.75	6	174.7341	175.3087	174.8467	175.6170	174.6843	170.9342	176.1175	176.4141	175.7996	172.7019	172.8036	171.3926
	1	8.25	21	174.6896	175.3005	174.8164	175.5312	174.6170	170.9240	176.0671	176.3328	175.7263	172.6970	172.7989	171.3249
	1	17.50	30	174.6912	175.3041	174.8188	175.4911	174.5959	170.9260	176.0540	176.3102	175.7195	172.7018	172.8041	171.3003
	2	11.00	48	174.6854	175.3013	174.8136	175.4433	174.5555	170.9204	176.0333	176.2711	175.7078	172.7025	172.8048	171.2619
	3	14.00	75	174.6763	175.2963	174.8043	175.4337	174.5449	170.9145	176.0214	176.2236	175.7036	172.7040	172.8073	171.2329
	4	14.50	99	174.6581	175.2847	174.7895	175.4245	174.5368	170.9037	176.0155	176.1890	175.6998	172.7050	172.9093	171.2118
	5	15.90	124	174.6304	175.2585	174.7606	175.4039	174.5160	170.8773	176.0031	176.1651	175.6894	172.7028	172.8065	171.1873
	7	11.10	168	174.5735	175.2061	174.7037	175.3581	174.4679	170.8250	175.9727	176.1260	175.6621	172.6935	172.7993	171.1456
	8	17.20	198	174.5288	175.1640	174.6607	175.3192	174.4276	170.7824	175.9444	176.0948	175.6353	172.6828	172.7889	171.1239
	10	10.24	239	174.4573	175.0956	174.5911	175.2528	174.3601	170.7124	175.8917	176.0388	175.5842	172.6561	172.7635	171.0850
	12	12.10	289	174.3745	175.0162	174.5126	175.1728	174.2789	170.6291	175.8256	175.9692	175.5198	172.6225	172.7296	171.0424
	14	16.75	341	174.2821	174.9281	174.4257	175.0838	174.1884	170.5367	175.7475	175.8879	175.4435	172.5797	172.6908	171.0005
	18	8.25	429	174.1145	174.7732	174.2739	174.9236	174.0272	170.3738	175.6047	175.7392	175.3034	172.4905	172.6040	170.9181
	21	13.90	506	173.9782	174.6449	174.1492	174.7908	173.8927	170.2399	175.4859	175.6175	175.1875	172.4158	172.5329	170.8525
	25	12.80	601	173.8006	174.4782	173.9874	174.6170	173.7173	170.0639	175.3309	175.4586	175.0363	172.3149	172.4355	170.7639
	29	14.35	699	173.6188	174.3037	173.8184	174.4338	173.5328	169.8802	175.1706	175.2936	174.8794	172.2078	172.3324	170.6700
01.09.2000	32	16.25	773	173.4764	174.1637	173.6854	174.2894	173.3879	169.7358	175.0447	175.1663	174.7572	172.1236	172.2509	170.5960
	37	8.50	885	173.2745	173.9669	173.4972	174.0843	173.1806	169.5291	174.8631	174.9816	174.5806	172.0044	172.1386	170.4942
12.09.2000	43	8.25	1029	173.0167	173.7120	173.2515	173.8181	172.9123	169.2611	174.6308	174.7441	174.3494	171.8535	171.9926	170.3625
16.09.2000	47	10.80	1127	172.8512	173.5476	173.0936	173.6473	172.7384	169.0878	174.4845	174.5944	174.2038	171.7642	171.9067	170.2843

Experiment 7 - Raw data

Alcohol				1-Propanol	1-Propanol	1-Propanol	1-Butanol	1-Butanol	1-Butanol	1-Hexanol	1-Hexanol	1-Hexanol	1-Octanol	1-Octanol	1-Octanol
Film thickness		mm		2.971	2.962	3.004	2.980	2.976	3.024	3.001	2.975	2.980	3.032	3.046	3.004
Mass (g)															
Date	Day	Hour	Time	A1	A2	A3	B1	B2	B3	C1	C2	C3	D1	D2	D3
16.09.2000	0	13.00	0	171.9155	172.5488	171.7034	172.0498	171.5936	167.9314	173.1821	173.3054	172.8473	170.5441	170.5310	169.3907
	1	10.80	22	171.8338	172.4152	171.5772	171.9401	171.5897	167.8811	173.1809	173.2912	172.8440	170.5440	170.5308	169.3869
	2	12.85	48	171.8149	172.3551	171.5492	171.9325	171.5853	167.8709	173.1806	173.2795	172.8410	170.5449	170.5318	169.3827
	3	14.25	73	171.8045	172.2909	171.5282	171.9221	171.5778	167.8629	173.1780	173.2720	172.8365	170.5540	170.5314	169.3772
	4	15.70	99	171.7906	172.2631	171.5134	171.9084	171.5664	167.8531	173.1762	173.2667	172.8334	170.5455	170.5328	169.3741
22.09.2000	6	10.90	142	171.7517	172.2238	171.4771	171.8664	171.5285	167.8186	173.1641	173.2498	172.8199	170.5458	170.5243	169.3690
	7	15.10	170	171.7175	172.1896	171.4430	171.8274	171.4918	167.7831	173.1467	173.2293	172.8021	170.5417	170.5123	169.3629
	9	12.90	216	171.6537	172.1241	171.3815	171.7518	171.4195	167.7119	173.1041	173.1833	172.7598	170.5236	170.4776	169.3471
28.09.2000	12	13.50	289	171.5427	172.0108	171.2711	171.6177	171.2893	167.5813	173.0125	173.0885	172.6682	170.4737	170.4022	169.3091
02.10.2000	16	10.50	382	171.3935	171.8575	171.1230	171.4362	171.1131	167.4038	172.8723	172.9459	172.5242	170.3813	170.2854	169.2433
05.10.2000	19	17.40	460	171.2782	171.7344	171.0041	171.2899	170.9704	167.2596	172.7536	172.8292	172.4005	170.2962	170.1878	169.1861
09.10.2000	23	8.00	547	171.1361	171.5947	170.8688	171.1235	170.8085	167.0972	172.6144	172.6960	172.2595	170.1946	170.0785	169.1187
12.10.2000	26	17.00	628	171.0092	171.4656	170.7437	170.9691	170.6570	166.9445	172.4830	172.5718	172.1253	170.0966	169.9767	169.0541
16.10.2000	30	16.25	723	170.8551	171.3090	170.5903	170.7810	170.4720	166.7578	172.3192	172.4180	171.9601	169.9722	169.8463	168.9712

APPENDIX B – RESULTS OF RELEASE TESTS



Release tests - 1-Propanol

Date	Day	Hour	Time	Dispenser mass						% of original mass						Average %	
				Round 1	Round 2	Round 3	Square 1	Square 2	Square 3	Round 1	Round 2	Round 3	Square 1	Square 2	Square 3	Round	Square
19.04.2000	0	9.40	0.0	10.06555	10.12210	10.15455	6.28235	6.39625	6.40140	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	0	16.33	6.9	9.84804	9.90374	9.95568	6.09392	6.17464	6.20482	97.8	97.8	98.0	97.0	96.5	96.9	97.9	96.8
	1	12.45	27.1	9.63477	9.69955	9.76617	5.92340	5.98942	6.03257	95.7	95.8	96.2	94.3	93.6	94.2	95.9	94.1
	2	12.90	51.5	9.49442	9.56502	9.63985	5.83982	5.90018	5.94771	94.3	94.5	94.9	93.0	92.2	92.9	94.6	92.7
	3	15.70	78.3	9.39098	9.46530	9.54535	5.79549	5.85305	5.90226	93.3	93.5	94.0	92.3	91.5	92.2	93.6	92.0
	5	10.95	121.6	9.28944	9.36725	9.45158	5.76617	5.82213	5.87213	92.3	92.5	93.1	91.8	91.0	91.7	92.6	91.5
	7	16.65	175.3	9.22700	9.30650	9.39305	5.75484	5.81009	5.86103	91.7	91.9	92.5	91.6	90.8	91.6	92.0	91.3
28.04.2000	9	16.20	222.8	9.19722	9.27784	9.36513	5.75178	5.80688	5.85714	91.4	91.7	92.2	91.6	90.8	91.5	91.8	91.3
02.05.2000	13	8.05	310.7	9.17237	9.25331	9.34163	5.75038	5.80530	5.85561	91.1	91.4	92.0	91.5	90.8	91.5	91.5	91.3
05.05.2000	16	16.45	391.1	9.16269	9.24401	9.33215	5.74970	5.80457	5.85479	91.0	91.3	91.9	91.5	90.7	91.5	91.4	91.2
09.05.2000	20	9.10	479.7	9.15666	9.23815	9.32641	5.74894	5.80386	5.85411	91.0	91.3	91.8	91.5	90.7	91.5	91.4	91.2
	23	17.10	559.7	9.15486	9.23634	9.32460	5.74879	5.80375	5.85384	91.0	91.2	91.8	91.5	90.7	91.4	91.3	91.2
	27	9.60	648.2	9.15260	9.23411	9.32228	5.74783	5.80281	5.85293	90.9	91.2	91.8	91.5	90.7	91.4	91.3	91.2

Release tests - 1-Butanol

Date	Day	Hour	Time	Dispenser mass						% of original mass						Average %	
				Round 1	Round 2	Round 3	Square 1	Square 2	Square 3	Round 1	Round 2	Round 3	Square 1	Square 2	Square 3	Round	Square
19.04.2000	0	9.50	0.0	10.09630	10.10655	10.17305	6.28335	6.42185	6.41430	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	0	16.40	6.9	9.89707	9.92502	9.97615	6.12945	6.20681	6.22379	98.0	98.2	98.1	97.6	96.7	97.0	98.1	97.1
	1	12.55	27.1	9.69766	9.74505	9.78685	5.97790	6.02252	6.05198	96.1	96.4	96.2	95.1	93.8	94.4	96.2	94.4
	2	12.95	51.5	9.56299	9.62251	9.65930	5.89648	5.92731	5.95389	94.7	95.2	94.9	93.8	92.3	92.8	95.0	93.0
	3	15.75	78.3	9.45986	9.52600	9.55703	5.84798	5.87177	5.89016	93.7	94.3	93.9	93.1	91.4	91.8	94.0	92.1
	5	11.00	121.5	9.35426	9.42423	9.44238	5.81100	5.82956	5.83463	92.7	93.2	92.8	92.5	90.8	91.0	92.9	91.4
	7	16.65	175.2	9.28344	9.35222	9.35485	5.79296	5.80884	5.80228	91.9	92.5	92.0	92.2	90.5	90.5	92.1	91.0
28.04.2000	9	16.20	222.7	9.24731	9.31390	9.30466	5.78668	5.80147	5.78836	91.6	92.2	91.5	92.1	90.3	90.2	91.7	90.9
02.05.2000	13	8.15	310.7	9.21326	9.27550	9.25080	5.78200	5.79564	5.77658	91.3	91.8	90.9	92.0	90.2	90.1	91.3	90.8
05.05.2000	16	16.50	391.0	9.19774	9.25672	9.22189	5.78062	5.79380	5.77202	91.1	91.6	90.7	92.0	90.2	90.0	91.1	90.7
09.05.2000	20	9.15	479.7	9.18782	9.24393	9.20126	5.77960	5.79265	5.76966	91.0	91.5	90.4	92.0	90.2	89.9	91.0	90.7
	23	17.15	559.7	9.18356	9.23836	9.19191	5.77915	5.79214	5.76873	91.0	91.4	90.4	92.0	90.2	89.9	90.9	90.7
	27	9.65	648.2	9.18031	9.23430	9.18570	5.77832	5.79127	5.76762	90.9	91.4	90.3	92.0	90.2	89.9	90.9	90.7

Release tests - 1-Hexanol

Date	Day	Hour	Time	Dispenser mass						% of original mass						Average %	
				Round 1	Round 2	Round 3	Square 1	Square 2	Square 3	Round 1	Round 2	Round 3	Square 1	Square 2	Square 3	Round	Square
19.04.2000	0	9.60	0.0	10.12880	10.13875	10.14640	6.37770	6.36695	6.36110	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	0	16.50	6.9	9.92026	9.91786	9.93079	6.19118	6.15790	6.17789	97.9	97.8	97.9	97.1	96.7	97.1	97.9	97.0
	1	12.60	27.0	9.72778	9.71475	9.73275	6.02363	5.97218	6.01182	96.0	95.8	95.9	94.4	93.8	94.5	95.9	94.3
	2	13.05	51.5	9.59563	9.57544	9.59798	5.92687	5.86665	5.91662	94.7	94.4	94.6	92.9	92.1	93.0	94.6	92.7
	3	15.80	78.2	9.48966	9.46394	9.49086	5.86541	5.80031	5.85653	93.7	93.3	93.5	92.0	91.1	92.1	93.5	91.7
	5	11.05	121.5	9.37195	9.34144	9.37382	5.81341	5.74520	5.80618	92.5	92.1	92.4	91.2	90.2	91.3	92.3	90.9
	7	16.70	175.1	9.28653	9.25279	9.28993	5.78621	5.71648	5.77992	91.7	91.3	91.6	90.7	89.8	90.9	91.5	90.5
28.04.2000	9	16.25	222.7	9.23885	9.20379	9.24353	5.77510	5.70498	5.76939	91.2	90.8	91.1	90.6	89.6	90.7	91.0	90.3
02.05.2000	13	8.15	310.6	9.19000	9.15372	9.19642	5.76655	5.69617	5.76139	90.7	90.3	90.6	90.4	89.5	90.6	90.6	90.2
05.05.2000	16	16.55	391.0	9.16511	9.12844	9.17276	5.76381	5.69334	5.75873	90.5	90.0	90.4	90.4	89.4	90.5	90.3	90.1
09.05.2000	20	9.25	479.7	9.14779	9.11084	9.15628	5.76171	5.69122	5.75673	90.3	89.9	90.2	90.3	89.4	90.5	90.1	90.1
	23	17.20	559.6	9.14024	9.10317	9.14934	5.76151	5.69098	5.75648	90.2	89.8	90.2	90.3	89.4	90.5	90.1	90.1
	27	9.70	648.1	9.13505	9.09808	9.14447	5.76064	5.69018	5.75569	90.2	89.7	90.1	90.3	89.4	90.5	90.0	90.1

Release tests - 1-Octanol

Date	Day	Hour	Time	Dispenser mass						% of original mass						Average %	
				Round 1	Round 2	Round 3	Square 1	Square 2	Square 3	Round 1	Round 2	Round 3	Square 1	Square 2	Square 3	Round	Square
19.04.2000	0	9.70	0.0	10.17085	10.17425	10.17400	6.38175	6.37895	6.36585	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	0	16.55	6.9	10.01990	10.03438	10.04156	6.23434	6.24628	6.24587	98.5	98.6	98.7	97.7	97.9	98.1	98.6	97.9
	1	12.65	27.0	9.83585	9.85785	9.88977	6.06638	6.09215	6.11065	96.7	96.9	97.2	95.1	95.5	96.0	96.9	95.5
	2	13.10	51.4	9.70843	9.73741	9.78519	5.96001	5.99457	6.02635	95.5	95.7	96.2	93.4	94.0	94.7	95.8	94.0
	3	15.85	78.2	9.60294	9.63688	9.69854	5.88527	5.92504	5.96563	94.4	94.7	95.3	92.2	92.9	93.7	94.8	92.9
	5	11.10	121.4	9.47673	9.51778	9.59288	5.81452	5.85852	5.90694	93.2	93.5	94.3	91.1	91.8	92.8	93.7	91.9
	7	16.75	175.1	9.37403	9.41936	9.50879	5.77097	5.81772	5.87073	92.2	92.6	93.5	90.4	91.2	92.2	92.7	91.3
28.04.2000	9	16.30	222.6	9.31249	9.36033	9.45753	5.75126	5.79913	5.85383	91.6	92.0	93.0	90.1	90.9	92.0	92.2	91.0
02.05.2000	13	8.20	310.5	9.24360	9.29433	9.40026	5.73443	5.78323	5.83946	90.9	91.4	92.4	89.9	90.7	91.7	91.5	90.7
05.05.2000	16	16.60	390.9	9.20489	9.25707	9.36775	5.72807	5.77714	5.83389	90.5	91.0	92.1	89.8	90.6	91.6	91.2	90.7
09.05.2000	20	9.30	479.6	9.17689	9.23009	9.34362	5.72403	5.77325	5.83035	90.2	90.7	91.8	89.7	90.5	91.6	90.9	90.6
	23	17.25	559.6	9.16446	9.21852	9.33344	5.72322	5.77243	5.82952	90.1	90.6	91.7	89.7	90.5	91.6	90.8	90.6
	27	9.75	648.1	9.15621	9.21089	9.32633	5.72220	5.77131	5.82845	90.0	90.5	91.7	89.7	90.5	91.6	90.7	90.6

APPENDIX C – RESULTS FROM MODELLING

Release modelling - 1-Propanol / Square samples

M0	g	6.36000	<div>$M = M_0 + \frac{8ALC_0}{\pi^2} \left[\left(\exp\left(\frac{-\pi^2 t D}{L^2}\right) - 1 \right) + \frac{1}{9} \left(\exp\left(\frac{-9\pi^2 t D}{L^2}\right) - 1 \right) + \frac{1}{25} \left(\exp\left(\frac{-25\pi^2 t D}{L^2}\right) - 1 \right) + \dots \right]$$= M_0 + X[A + B + C + D + E]$</div>											
Mf	g	5.80119												
Ms	g	0.55881												
Side length	mm	59.00000												
Thickness	mm	2.00000												
Area	mm^2	3481												
Volume	mm^3	6962												
C0	g/mm^3	0.00008												
D	mm^2/h	0.01322												
X	g	0.45296												
	% of original mass		Dispenser mass			Release rate		Term	1	9	25	49	81	
Time	Exp C3S	Mod C3S	Exp C3S	Mod C3S	Time	Exp C3S	Mod C3S	X	A	B	C	D	E	Difs
h	%	%	g	g	h	g/h	g/h	g						%
0.00	100.00	100.00	6.3600	6.3600				0.45296	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
6.93	96.82	97.35	6.1578	6.1917	3	0.02918	0.02428	0.45296	-0.20232	-0.09658	-0.03986	-0.02041	-0.01235	0.53239
27.05	94.05	94.52	5.9818	6.0112	17	0.00875	0.00897	0.45296	-0.58619	-0.11107	-0.04000	-0.02041	-0.01235	0.46127
51.50	92.70	92.90	5.8959	5.9082	39	0.00351	0.00421	0.45296	-0.81360	-0.11111	-0.04000	-0.02041	-0.01235	0.19177
78.30	91.99	92.12	5.8503	5.8590	65	0.00170	0.00184	0.45296	-0.92224	-0.11111	-0.04000	-0.02041	-0.01235	0.13559
121.55	91.51	91.70	5.8201	5.8324	100	0.00070	0.00062	0.45296	-0.98103	-0.11111	-0.04000	-0.02041	-0.01235	0.19046
175.25	91.33	91.59	5.8087	5.8253	148	0.00021	0.00013	0.45296	-0.99671	-0.11111	-0.04000	-0.02041	-0.01235	0.25947
222.80	91.28	91.57	5.8053	5.8241	199	0.00007	0.00002	0.45296	-0.99930	-0.11111	-0.04000	-0.02041	-0.01235	0.29420
310.65	91.26	91.57	5.8038	5.8238	267	0.00002	0.00000	0.45296	-0.99996	-0.11111	-0.04000	-0.02041	-0.01235	0.31314
391.05	91.24	91.57	5.8030	5.8238	351	0.00001	0.00000	0.45296	-1.00000	-0.11111	-0.04000	-0.02041	-0.01235	0.32456
479.70	91.23	91.57	5.8023	5.8238	435	0.00001	0.00000	0.45296	-1.00000	-0.11111	-0.04000	-0.02041	-0.01235	0.33581
559.70	91.23	91.57	5.8021	5.8238	520	0.00000	0.00000	0.45296	-1.00000	-0.11111	-0.04000	-0.02041	-0.01235	0.33859
648.20	91.22	91.57	5.8012	5.8238	604	0.00001	0.00000	0.45296	-1.00000	-0.11111	-0.04000	-0.02041	-0.01235	0.35332

Release modelling- 1-Butanol / Square samples

M0	g	6.37317	$M = M_0 + \frac{8ALC_0}{\pi^2} \left[\left(\exp\left(\frac{-\pi^2 tD}{L^2}\right) - 1 \right) + \frac{1}{9} \left(\exp\left(\frac{-9\pi^2 tD}{L^2}\right) - 1 \right) + \frac{1}{25} \left(\exp\left(\frac{-25\pi^2 tD}{L^2}\right) - 1 \right) + \right]$											
Mf	g	5.77907	$= M_0 + X[A + B + C + D + E]$											
Ms	g	0.59410												
Side length	mm	59.00000												
Thickness	mm	2.00000												
Area	mm^2	3481												
Volume	mm^3	6962												
C0	g/mm^3	0.00009												
D	mm^2/h	0.01154												
X	g	0.48156												
% of original mass			Dispenser mass		Release rate			Term	1	9	25	49	81	
Time	Exp C4S	Mod C4S	Exp C4S	Mod C4S	Time	Exp C4S	Mod C4S	X	A	B	C	D	E	Difs
h	%	%	g	g	h	g/h	g/h	g						%
0.00	100.00	100.00	6.3732	6.3732				0.48156	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
6.90	97.08	97.41	6.1867	6.2080	3	0.02703	0.02394	0.48156	-0.17837	-0.09215	-0.03971	-0.02041	-0.01235	0.33108
27.05	94.42	94.55	6.0175	6.0260	17	0.00840	0.00903	0.48156	-0.53709	-0.11100	-0.04000	-0.02041	-0.01235	0.12936
51.45	92.99	92.80	5.9259	5.9143	39	0.00375	0.00458	0.48156	-0.76892	-0.11111	-0.04000	-0.02041	-0.01235	-0.18728
78.25	92.11	91.87	5.8700	5.8549	65	0.00209	0.00222	0.48156	-0.89226	-0.11111	-0.04000	-0.02041	-0.01235	-0.24254
121.50	91.41	91.29	5.8251	5.8182	100	0.00104	0.00085	0.48156	-0.96856	-0.11111	-0.04000	-0.02041	-0.01235	-0.11515
175.15	91.04	91.11	5.8014	5.8064	148	0.00044	0.00022	0.48156	-0.99318	-0.11111	-0.04000	-0.02041	-0.01235	0.07019
222.70	90.89	91.07	5.7922	5.8039	199	0.00019	0.00005	0.48156	-0.99824	-0.11111	-0.04000	-0.02041	-0.01235	0.17585
310.65	90.78	91.06	5.7847	5.8031	267	0.00008	0.00001	0.48156	-0.99986	-0.11111	-0.04000	-0.02041	-0.01235	0.27993
391.00	90.74	91.05	5.7821	5.8031	351	0.00003	0.00000	0.48156	-0.99999	-0.11111	-0.04000	-0.02041	-0.01235	0.31952
479.65	90.71	91.05	5.7806	5.8031	435	0.00002	0.00000	0.48156	-1.00000	-0.11111	-0.04000	-0.02041	-0.01235	0.34306
559.65	90.70	91.05	5.7800	5.8031	520	0.00001	0.00000	0.48156	-1.00000	-0.11111	-0.04000	-0.02041	-0.01235	0.35292
648.15	90.69	91.05	5.7791	5.8031	604	0.00001	0.00000	0.48156	-1.00000	-0.11111	-0.04000	-0.02041	-0.01235	0.36761

Release modelling - 1-Hexanol / Square samples

M0	g	6.36858	$M = M_0 + \frac{8ALC_0}{\pi^2} \left[\left(\exp\left(\frac{-\pi^2 tD}{L^2}\right) - 1 \right) + \frac{1}{9} \left(\exp\left(\frac{-9\pi^2 tD}{L^2}\right) - 1 \right) + \frac{1}{25} \left(\exp\left(\frac{-25\pi^2 tD}{L^2}\right) - 1 \right) + \dots \right]$ $= M_0 + X[A + B + C + D + E]$											
Mf	g	5.73550												
Ms	g	0.63308												
Side length	mm	59.00000												
Thickness	mm	2.00000												
Area	mm^2	3481												
Volume	mm^3	6962												
C0	g/mm^3	0.00009												
D	mm^2/h	0.00822												
X	g	0.51316												
												</		

Release modelling - 1-Propanol / Round samples

M0	g	10.11407	$M = M_0 + \frac{8ALC_0}{\pi^2} \left[\left(\exp\left(\frac{-\pi^2 tD}{L^2}\right) - 1 \right) + \frac{1}{9} \left(\exp\left(\frac{-9\pi^2 tD}{L^2}\right) - 1 \right) + \frac{1}{25} \left(\exp\left(\frac{-25\pi^2 tD}{L^2}\right) - 1 \right) + \dots \right]$											
Mf	g	9.23633	$= M_0 + X[A + B + C + D + E]$											
Ms	g	0.87774												
Diameter	mm	67.5												
Thickness	mm	3.0												
Area	mm^2	3578												
Volume	mm^3	10735												
C0	g/mm^3	0.00008												
D	mm^2/h	0.01322												
X	g	0.71147												
% of original mass			Dispenser mass		Release rate			Term	1	9	25	49	81	
Time	Exp C3R	Mod C3R	Exp C3R	Mod C3R	Time	Exp C3R	Mod C3R	X	A	B	C	D	E	Difs
h	%	%	g	g	h	g/h	g/h	g						%
0.00	100.00	100.00	10.1141	10.1141				0.71147	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
6.93	97.91	98.37	9.9025	9.9497	3	0.03053	0.02372	0.71147	-0.09558	-0.06613	-0.03675	-0.02026	-0.01234	0.46678
27.05	95.91	96.45	9.7002	9.7548	17	0.01006	0.00969	0.71147	-0.32440	-0.10785	-0.04000	-0.02041	-0.01235	0.54057
51.50	94.58	95.01	9.5664	9.6091	39	0.00547	0.00596	0.71147	-0.52603	-0.11098	-0.04000	-0.02041	-0.01235	0.42268
78.30	93.60	93.93	9.4672	9.5004	65	0.00370	0.00405	0.71147	-0.67862	-0.11111	-0.04000	-0.02041	-0.01235	0.32952
121.55	92.64	92.88	9.3694	9.3939	100	0.00226	0.00246	0.71147	-0.82832	-0.11111	-0.04000	-0.02041	-0.01235	0.24339
175.25	92.04	92.23	9.3089	9.3279	148	0.00113	0.00123	0.71147	-0.92119	-0.11111	-0.04000	-0.02041	-0.01235	0.18913
222.80	91.75	91.95	9.2801	9.2999	199	0.00061	0.00059	0.71147	-0.96044	-0.11111	-0.04000	-0.02041	-0.01235	0.19763
310.65	91.51	91.75	9.2558	9.2797	267	0.00028	0.00023	0.71147	-0.98893	-0.11111	-0.04000	-0.02041	-0.01235	0.23744
391.05	91.42	91.70	9.2463	9.2742	351	0.00012	0.00007	0.71147	-0.99655	-0.11111	-0.04000	-0.02041	-0.01235	0.27765
479.70	91.36	91.68	9.2404	9.2725	435	0.00007	0.00002	0.71147	-0.99905	-0.11111	-0.04000	-0.02041	-0.01235	0.31820
559.70	91.34	91.67	9.2386	9.2720	520	0.00002	0.00001	0.71147	-0.99970	-0.11111	-0.04000	-0.02041	-0.01235	0.33146
648.20	91.32	91.67	9.2363	9.2718	604	0.00003	0.00000	0.71147	-0.99992	-0.11111	-0.04000	-0.02041	-0.01235	0.35238

Release modelling - 1-Octanol / Round samples

M0	g	10.17303	<div>$M = M_0 + \frac{8ALC_0}{\pi^2} \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) + \right]$$= M_0 + X[A + B + C + D + E]$</div>											
Mf	g	9.23114												
Ms	g	0.94189												
Diameter	mm	67.5												
Thickness	mm	3.0												
Area	mm^2	3578												
Volume	mm^3	10735												
C0	g/mm^3	0.00009												
D	mm^2/h	0.00616												
X	g	0.76347												
	% of original mass		Dispenser mass			Release rate		Term	1	9	25	49	81	
Time	Exp C8R	Mod C8R	Exp C8R	Mod C8R	Time	Exp C6R	Mod C6R	X	A	B	C	D	E	Difs
h	%	%	g	g	h	g/h	g/h	g						%
0.00	100.00	100.00	10.1730	10.1730				0.76347	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
6.85	98.61	98.94	10.0319	10.0655	3	0.02060	0.01570	0.76347	-0.04522	-0.03785	-0.02742	-0.01829	-0.01205	0.32994
26.95	96.93	97.54	9.8612	9.9224	17	0.00850	0.00712	0.76347	-0.16644	-0.08952	-0.03958	-0.02041	-0.01235	0.60194
51.40	95.78	96.46	9.7437	9.8124	39	0.00480	0.00450	0.76347	-0.29335	-0.10623	-0.03999	-0.02041	-0.01235	0.67586
78.15	94.82	95.55	9.6461	9.7202	65	0.00365	0.00345	0.76347	-0.41017	-0.11015	-0.04000	-0.02041	-0.01235	0.72864
121.40	93.67	94.42	9.5291	9.6055	100	0.00270	0.00265	0.76347	-0.55960	-0.11104	-0.04000	-0.02041	-0.01235	0.75048
175.05	92.74	93.42	9.4341	9.5032	148	0.00177	0.00191	0.76347	-0.69349	-0.11111	-0.04000	-0.02041	-0.01235	0.67974
222.60	92.17	92.78	9.3768	9.4389	199	0.00120	0.00135	0.76347	-0.77769	-0.11111	-0.04000	-0.02041	-0.01235	0.61079
310.50	91.54	92.04	9.3127	9.3629	267	0.00073	0.00086	0.76347	-0.87724	-0.11111	-0.04000	-0.02041	-0.01235	0.49340
390.90	91.19	91.65	9.2766	9.3236	351	0.00045	0.00049	0.76347	-0.92868	-0.11111	-0.04000	-0.02041	-0.01235	0.46275
479.60	90.93	91.41	9.2502	9.2991	435	0.00030	0.00028	0.76347	-0.96083	-0.11111	-0.04000	-0.02041	-0.01235	0.48072
559.55	90.82	91.29	9.2388	9.2866	520	0.00014	0.00016	0.76347	-0.97717	-0.11111	-0.04000	-0.02041	-0.01235	0.47004
648.05	90.74	91.21	9.2311	9.2788	604	0.00009	0.00009	0.76347	-0.98745	-0.11111	-0.04000	-0.02041	-0.01235	0.46828

Release modelling - 1-Hexanol / Round samples

M0	g	10.13798	$M = M_0 + \frac{8ALC_0}{\pi^2} \left[\left(\exp\left(\frac{-\pi^2 tD}{L^2}\right) - 1 \right) + \frac{1}{9} \left(\exp\left(\frac{-9\pi^2 tD}{L^2}\right) - 1 \right) + \frac{1}{25} \left(\exp\left(\frac{-25\pi^2 tD}{L^2}\right) - 1 \right) + \dots \right]$ $= M_0 + X[A + B + C + D + E]$												
Mf	g	9.12587													
Ms	g	1.01212													
Diameter	mm	67.5													
Thickness	mm	3.0													
Area	mm^2	3578													
Volume	mm^3	10735													
C0	g/mm^3	0.00009													
D	mm^2/h	0.00822													
X	g	0.82039													

Release modelling - 1-Octanol / Round samples

M0	g	10.17303	$M = M_0 + \frac{8ALC_0}{\pi^2} \left[\left(\exp\left(\frac{-\pi^2 tD}{L^2}\right) - 1 \right) + \frac{1}{9} \left(\exp\left(\frac{-9\pi^2 tD}{L^2}\right) - 1 \right) + \frac{1}{25} \left(\exp\left(\frac{-25\pi^2 tD}{L^2}\right) - 1 \right) + \right]$ $= M_0 + X[A + B + C + D + E]$												
Mf	g	9.23114													
Ms	g	0.94189													
Diameter	mm	67.5													
Thickness	mm	3.0													
Area	mm^2	3578													
Volume	mm^3	10735													
C0	g/mm^3	0.00009													
D	mm^2/h	0.00616													
X	g	0.76347													
			% of original mass		Dispenser mass		Release rate		Term	1	9	25	49	81	
Time	Exp C8R	Mod C8R	Exp C8R	Mod C8R	Time	Exp C6R	Mod C6R	X	A	B	C	D	E	Difs	
h	%	%	g	g	h	g/h	g/h	g							%
0.00	100.00	100.00	10.1730	10.1730				0.76347	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
6.85	98.61	98.94	10.0319	10.0655	3	0.02060	0.01570	0.76347	-0.04522	-0.03785	-0.02742	-0.01829	-0.01205	0.32994	
26.95	96.93	97.54	9.8612	9.9224	17	0.00850	0.00712	0.76347	-0.16644	-0.08952	-0.03958	-0.02041	-0.01235	0.60194	
51.40	95.78	96.46	9.7437	9.8124	39	0.00480	0.00450	0.76347	-0.29335	-0.10623	-0.03999	-0.02041	-0.01235	0.67586	
78.15	94.82	95.55	9.6461	9.7202	65	0.00365	0.00345	0.76347	-0.41017	-0.11015	-0.04000	-0.02041	-0.01235	0.72864	
121.40	93.67	94.42	9.5291	9.6055	100	0.00270	0.00265	0.76347	-0.55960	-0.11104	-0.04000	-0.02041	-0.01235	0.75048	
175.05	92.74	93.42	9.4341	9.5032	148	0.00177	0.00191	0.76347	-0.69349	-0.11111	-0.04000	-0.02041	-0.01235	0.67974	
222.60	92.17	92.78	9.3768	9.4389	199	0.00120	0.00135	0.76347	-0.77769	-0.11111	-0.04000	-0.02041	-0.01235	0.61079	
310.50	91.54	92.04	9.3127	9.3629	267	0.00073	0.00086	0.76347	-0.87724	-0.11111	-0.04000	-0.02041	-0.01235	0.49340	
390.90	91.19	91.65	9.2766	9.3236	351	0.00045	0.00049	0.76347	-0.92868	-0.11111	-0.04000	-0.02041	-0.01235	0.46275	
479.60	90.93	91.41	9.2502	9.2991	435	0.00030	0.00028	0.76347	-0.96083	-0.11111	-0.04000	-0.02041	-0.01235	0.48072	
559.55	90.82	91.29	9.2388	9.2866	520	0.00014	0.00016	0.76347	-0.97717	-0.11111	-0.04000	-0.02041	-0.01235	0.47004	
648.05	90.74	91.21	9.2311	9.2788	604	0.00009	0.00009	0.76347	-0.98745	-0.11111	-0.04000	-0.02041	-0.01235	0.46828	