Release of additives from packaging plastics

Promotoren

Prof. dr. W.M.F. Jongen
Hoogleraar Productontwerpen en Kwaliteitskunde met bijzondere aandacht voor ketenaspecten, Wageningen Universiteit

Prof. ir. J.A. Wesselingh
Hoogleraar in de Fysische Technologie, Rijksuniversiteit Groningen

Co-promotor

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Universitair docent, leerstoelgroep Productontwerpen en Kwaliteitskunde, Wageningen Universiteit

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Dr. A. Feigenbaum (INRA, Reims, Frankrijk)
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Ingrid Erika Helmroth

Proefschrift
ter verkrijging van de graad van doctor
op gezag van de rector magnificus
van Wageningen Universiteit,
prof. dr. ir. L. Speelman,
in het openbaar te verdedigen
op dinsdag 12 november 2002
des namiddags te vier uur in de Aula.

ISBN: 90-5808-737-9

Abstract

Helmroth, I.E. (2002). Release of additives from packaging plastics. Ph.D. thesis, Wageningen University, The Netherlands.

The diffusion of small molecules from polymers into food is studied. A better understanding of this process is important for the development of mathematical models to predict migration from packaging plastics into food. To study the effect of food absorption by the plastic on diffusion, the simultaneous diffusion of a migrant (Irganox 1076) and a solvent in low density polyethylene (LDPE) were measured. The migrant diffuses out of the polymer, while the solvent is diffusing inwards. For solvents with low molar mass the diffusion coefficient of Irganox 1076 increases with increasing solvent uptake. No increase in diffusion coefficient was found upon uptake of tri-glycerides such as olive oil. A method using microtoming and GC-analysis is tested for the measurement of migrant concentration profiles inside the polymer. The diffusion of Irganox 1076 and solvent in LDPE have been measured as a function of time. The Fick equation with a migrant diffusivity depending on the solvent concentration gives a good description of the results for isooctane and *n*-heptane. The description is less good for the measurements with cyclohexane (when the polymer swells strongly). The use of predictive modelling for legislative purposes is evaluated for a deterministic, a worst-case and a new stochastic approach. All approaches give a reasonable, but rough, estimation of the diffusion coefficient. The new stochastic approach has the advantage that an entire probability distribution may be obtained.

Keywords: migration, diffusion, additives, polymer, low density polyethylene, polymer swelling, Fick, stochastic modelling

Contents

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Introduction

1.1 Problem definition

The use of materials such as paper, glass, metal and plastic in contact with food is widespread. Examples are packaging materials such as bottles, bags, boxes and wrappers, but also for example storage containers, crockery, bulk storage vessels, pallets and transport devices in food industry. When the material is inert, contact with food does not cause any problems. Otherwise interactions between contact material and food may occur. Then compounds, naturally present in the material or as a result of its production process, are transported into the food and influence its quality or even its safety for human health. In packaging science, the transport of compounds from a food contact material into a food product is called *migration*. In Europe, migration is regulated by EC Directives and, when these are absent, by national legislation. Materials that are in contact with food have to comply with these regulations. Therefore, certification laboratories and industry carry out large numbers of time-consuming and expensive migration experiments on new materials. Many migration experiments are also performed by governmental laboratories to enforce the migration regulations for randomly sampled food contact materials.

This thesis deals with migration from *plastics* (or *polymers*), materials that are largely used for food contact applications due to their low weight, low cost and excellent properties. A disadvantage of plastics is the presence of high amounts of possible migrants: polymer additives such as plasticisers and UV stabilisers, and other small molecules. Migration depends on the properties of plastic and migrant (how easily the migrant can move through the polymeric network), on the type of food (liquid or solid, fatty or aqueous) and on the temperature history of the packaging/food combination.

A better understanding of migration in plastics is important from both a fundamental and a practical point of view. Fundamental insight in the transport of molecules through polymers is the basis of many applications, including plastics for packaging materials, controlled release of pharmaceuticals and active packaging. In practice a reduction of the number of migration tests using predictive models of migration would save time and money for both industry and testing labs. Predictions require information about the rate of diffusion of the migrant in the polymer and the distribution of migrant between polymer and food. It is still very difficult to predict these values. A problem arises if the food or food simulant (a defined solvent replacing real food) is absorbed by the polymer and affects the diffusion of the migrants due to swelling of the polymer. If this effect is significant, then it must be included in a predictive model. There is, however, still a lack of knowledge about the significance of this effect and how it may be mathematically described.

1.2 Objectives

The objectives of this thesis are as follows:

1) To investigate the possible use of predictive modelling of migration for legislative purposes and to evaluate different modelling approaches.
2) To study the effect of solvent absorption by the plastic on additive migration. Of specific interest are the effects of food simulants and other solvents in low density polyethylene (LDPE).

1.3 Outline

This thesis consists of two parts according to the two objectives. Chapter 2 gives a review of migration theory and an evaluation of migration models suggested for legislative use. A new approach for the prediction of migration using probabilistic modelling is presented in Chapter 3. Chapter 4 shows results of the effect of solvent absorption on additive migration from LDPE into food simulants and other solvents by measuring of migrant concentrations in the solvent. Chapter 5 evaluates a method for measuring additive concentration profiles directly in the plastic. In Chapter 6 the method is used to study additive migration and solvent absorption in LDPE for solvents that are highly absorbed by the polymer. Chapter 7 discusses the results obtained and gives recommendations for future research.

2

Modelling of migration for regulatory purposes[1]

Abstract

Migration of compounds with small molar mass is an important problem for packaging plastics and other plastics intended to come into contact with food. Since migration experiments are time consuming and expensive, predictive modelling has been introduced as an alternative. The objective of this article is to review current knowledge on migration modelling and to highlight the consequences of using modelling for regulatory purposes.

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[1] accepted as 'Predictive modelling of migration from packaging materials into food products for regulatory purposes', Erika Helmroth, Rinus Rijk, Matthijs Dekker and Wim Jongen, *Trends in Food Science and Technology*

2.1 Introduction

The migration of compounds into food is an important safety aspect of food packaging and other food contact plastics. Plastic additives used to improve polymer properties, and residual monomers or oligomers are not chemically bound to the polymer and can move freely within the polymer. Consequently they can dissolve in the food at the interface between packaging material and food. Table 2.1 lists some polymers commonly used in contact with food and gives examples of additives and monomers that are likely to migrate from the given plastic (Brydson, 1995, Brody & Marsh, 1997).

Depending on the toxicological properties of the migrants, migration is restricted by national and international food regulations. In Europe compounds authorized for use in food contact materials are listed in Commission Directive 90/128/EEC and its amendments (2001). Many of these compounds are provided with a specific migration limit (SML), which is a limit on the maximum quantity of the compound allowed to migrate into the food. To demonstrate compliance of a plastic with the limits, specific migration experiments are required. In these experiments, the plastic is brought into contact with a food simulant (vegetable oil, alcoholic, aqueous or acidic solution) for an established time and temperature (Council Directive, 1985, Commision Directive, 1997, Ashby, Cooper, Harvey & Tice, 1997, Hernandez & Gavara, 1999, Piringer & Baner, 2000).

As migration experiments are time-consuming, expensive and often difficult, the use of mathematical models to predict migration is gaining interest. Migration in polymers is known to follow physical diffusion laws. This opens the possibility of a mathematical description of migration and the use of such models for prediction. There is currently a discussion in Europe on basing approval of packaging materials on predictions instead of experiments. In the 6th amendment of the Commission Directive 90/128/EEC (2001) the use of 'generally recognized diffusion models' as an alternative test method has been approved. However, use of such a method by packaging companies, enforcement laboratories and certification institutes requires insight in the background of these models.

Table 2.1 Common polymers in food packaging applications including their glass transition temperature (T_g) and examples of migrants (Brydson, 1995, Brody & Marsh, 1997)

Polymer	T_g (°C)	Possible migrants	Food applications
Low density polyethylene (LDPE)	-20	Antioxidants^(a), antistatics^(a), pigments^(a), lubricants^(a), slip agents^(a)	Film, grocery bags, lids, coatings, squeeze bottles
High density polyethylene (HDPE)	-20	Same as LDPE	Bottles, caps and closures, grocery bags, cereal wrappers
Polypropylene (PP)	+5	Antioxidants^(a), pigments^(a), UV absorbers^(a)	Candy wraps, snack-food pouches, lids, margarine cups, closures
Polystyrene (PS)	+90-+100	Styrene^(m), UV absorbers^(a), High impact modifier^(a)	Meat and cookie trays, fast-food containers, bottles
Polyethylene terephthalate (APET)	+67	Terephthalic acid^(m) Cyclic PET trimer^(m), catalysts^(a)	Bottles, 'ovenable' trays
Polyvinylchloride (PVC)	+80	Stabilizers^(a), plasticizers^(a), pigments^(a) vinylchloride^(m)	Film for meat and cheese
Polycarbonate (PC)	+149	Bisphenol A^(m), Emulsifiers^(a), Antioxidants^(a)	Bottles, coatings, 'ovenable' trays

(a) additive

(m) monomer

The aim of this article is to review critically the current state of knowledge on predictive migration modelling for regulatory purposes. First basic theory on diffusion in polymers and modelling is treated, after which the applicability and consequences of different modelling approaches for regulatory purposes will be highlighted.

2.2 Physics of migration

How quickly and to what extent migration will occur is determined by the properties of migrant, polymer and food simulant and by the temperature. Migrants pass through voids and other gaps between the polymer molecules. So the migration rate will to a large extent depend on the size and shape of the migrants and on the size and number of the gaps. The latter will depend on polymer properties such as density, crystallinity and degree of crosslinking and branching. Also important is the glass transition temperature (T_g) of the polymer, which determines the flexibility of the polymer molecules. Below T_g, the polymer molecules are stiff (glassy) and the chance of a migrant finding a sufficiently large hole is limited. Above T_g, the polymer molecules are flexible (rubbery), which makes this chance higher. Therefore, in general, the lower the T_g of a polymer, the higher the migration rates. Irrespective of the T_g, the higher the temperature, the higher the flexibility of the polymer molecules and thus the higher the migration rates (Brydson, 1995).

Thermodynamic properties such as polarity and solubility influence the migration rate due to interactions between polymer, migrant and food simulant. For example, if a migrant has a poor solubility in the food simulant, it will rather remain in the polymer than migrate into the food simulant. This is often the case with apolar additives in apolar polymers, such as low-density polyethylene (LDPE), polypropylene (PP) and polystyrene (PS) in contact with polar food simulants such as water or 3% acetic acid. Higher migration rates are often found for fatty simulants, for example olive oil, 95% ethanol or isooctane (Till et al., 1987, Riquet & Feigenbaum, 1997, Linssen, Reitsema & Cozijnsen, 1998). If the food simulant itself has a high affinity for the polymer, then it may be absorbed by the polymer. Absorption of certain organic solvents causes swelling of the polymer, enlarging the gaps and increasing additive migration rates (Koszinowski, 1986, Reynier, Dole & Feigenbaum, 1999, Reynier, Dole & Feigenbaum, 2001, Helmroth, Dekker & Hankemeier, 2002). The effect of absorption of real foods and food simulants into the polymer matrix is not clear but may be important. An effect of oil absorption on migration was found in PP (Reynier, Dole & Feigenbaum, 2001), but not in LDPE (Helmroth, Dekker & Hankemeier, 2002).

2.3 Modelling approaches

Mathematical modelling may be carried out at different levels of description, for example *specific* versus *general*, *microscopic* versus *macroscopic* and *stochastic* versus *deterministic* (Gershenfeld, 1999).

Specific versus general

For one particular combination of polymer, migrant, food simulant and temperature, a *specific* model would be the most reliable. However, as the number of possible combinations is very large, this would be impossible. Therefore *general* models are developed that use relationships between physical properties and migration.

Microscopic versus macroscopic

Molecular simulation is a modelling technique that describes molecular movements using information about molecule geometry and interaction energies of polymer and migrant molecules (Theodorou, 1996). These *microscopic* models can generate accurate results for a given model system. However, due to its complexity this technique is currently not practical. *Macroscopic* models describe diffusion as a ‘black-box’ with a few model parameters in which many properties have been ‘lumped’.

Stochastic versus deterministic

Most models assume that migration is a *deterministic* process: for a given polymer, migrant, food simulant and temperature, the amount migrated at time *t* always has one specific value. However, in real life there will always be variation. In packaging/food combinations variation is always present due to heterogeneity of the composition and structure of food and packaging and uncertainty about the temperature history of the packaging/food combination (Chatwin & Katan, 1989). On a laboratory scale, variation is caused by measurement errors and differences in experimental set-up. *Stochastic* models, also called probabilistic models, take these variations into account by predicting the most probable outcome based on a large number of data from earlier experiments. The result is given as probability distributions showing which migration values are the most likely to occur in a given food/packaging combination and for a given time and temperature (Chatwin et al., 1989, Lum Wan, Chatwin & Katan, 1995, Petersen, 2000, Helmroth & Varekamp, submitted).

2.4 Diffusion equations

Most migration processes, whether they concern small or large molecules, into, through or out of a packaging material, can be described by the diffusion equations of Fick. Many books and reviews have appeared on the solution of these differential equations under specific conditions. The most extensive work is by Crank (1975), who has provided solutions for a large number of diffusion problems. Articles focussing on packaging often provide useful information on the assumptions under which appropriate equations apply (Crosby, 1981, Chatwin et al., 1989, Vergnaud, 1991, Lum Wan et al., 1995, , Vergnaud, 1995/6, Begley, 1997, Hamdani, Feigenbaum & Vergnaud, 1997, Lickly, Rainey, Burgert, Breder & Borodinsky, 1997, Piringer et al., 2000). Figure 2.1 illustrates the migration of a compound migrating from a packaging film into a food simulant based on the diffusion equations of Fick.

The key point of predicting migration is how to obtain values for the model parameters that are specific for each combination of migrant, polymer and food simulant. For migration prediction, usually models are used with two parameters: a diffusion coefficient and a partition coefficient. The diffusion coefficient (D) represents the migration rate and the partition coefficient (K) represents the ratio of the migrant concentration in the packaging to the migrant concentration in the food simulant at equilibrium. Figure 2.2 illustrates the effect of the model parameters on the migrant concentration in the food simulant as a function of time, based on the diffusion equations of Fick.

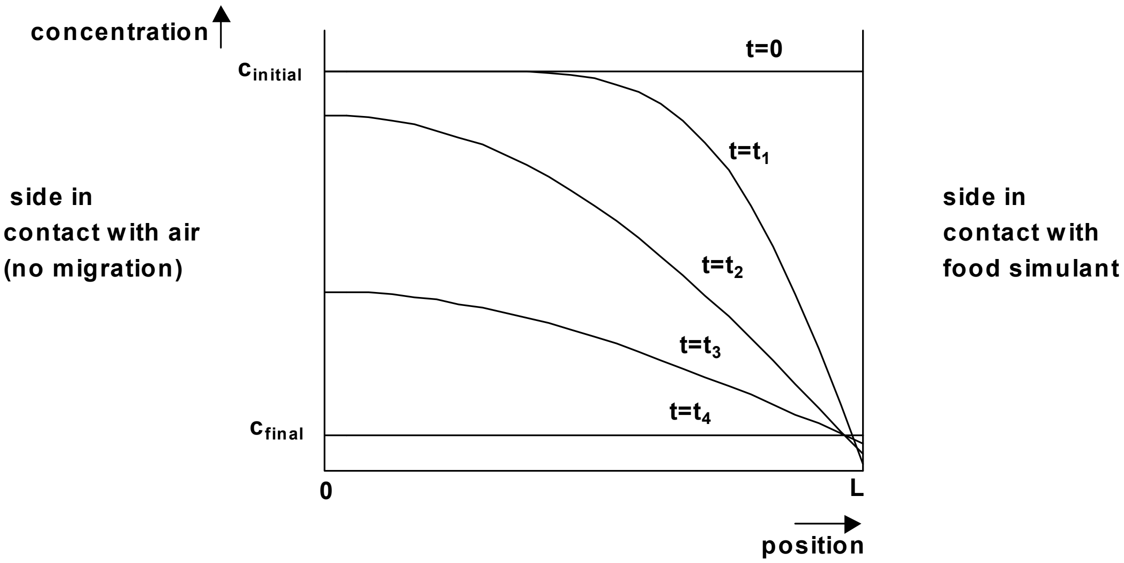

Figure 2.1 Profiles of concentration of migrant in plastic film with thickness *L* and one side in contact with food simulant after various incubation times.

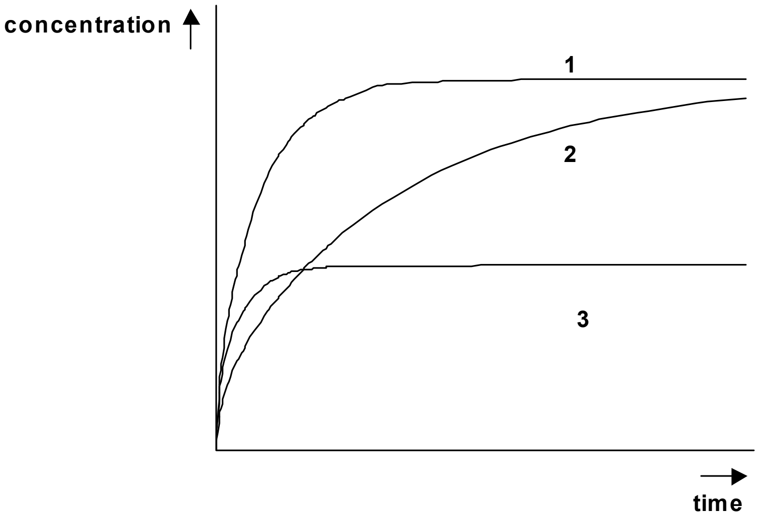

Figure 2.2 The effect of model parameters *D* and *K* on additive concentration in a food simulant caused by migration from a plastic film as a function of time. 1. $D = D_1$, $K = K_1$, 2. $D < D_1$, $K = K_1$, and 3. $D = D_1$, $K > K_1$ (according to definition of *K* in text).

2.5 Diffusion coefficient

One of the most successful theories for describing diffusion in polymers is the free-volume theory, which accounts for the probability of a migrant finding a neighbouring hole that is large enough for migration. However, equations for predicting a diffusion coefficient based on this theory include many adjustable parameters that are difficult to predict or measure other than for a few model systems (Duda, 1996, Hedenqvist, Angelstok, Edsberg, Larsson & Gedde, 1996, Ramesh & Duda, 2001, Tonge & Gilbert, 2001).

The dependency of the diffusion coefficient on temperature is described by the Arrhenius equation given by (Naylor, 1988)

$$D = D_0 \exp\left(-\frac{E}{RT}\right). \tag{2.1}$$

Here D_0 is a hypothetical diffusion coefficient at very high temperature ($m^2\ s^{-1}$), E is the activation energy of diffusion ($J\ mol^{-1}$), R the gas constant ($J\ mol^{-1}\ K^{-1}$) and T the temperature (K). D_0 and E can be obtained by fitting experimental data.

For practical applications, several semi-empirical equations of the diffusion coefficient as a function of the molar mass of the migrant and the temperature have been proposed. These are discussed below.

(1) *Deterministic approach*

The equation proposed by Limm and Hollifield (1996) for diffusion coefficient in polyolefins was developed from physical diffusion theories and is given by

$$D = D_0 \exp\left(\alpha M^{\frac{1}{2}} - \frac{KM^{\frac{1}{3}}}{T}\right) \tag{2.2}$$

where M is the molar mass (g mol^{-1}), T is the temperature (K) and D_0, α and K are adjustable parameters. These are specific for each polymer and were determined from diffusion coefficients calculated from migration data of the antioxidants Irganox 1010 and Irganox 1076 from PP, HDPE (high density polyethylene) and LDPE to corn oil. The model was tested on a large number (113) of diffusion coefficients found in literature and was on average found to give predictions differing between around 2 times too low and 8 times too high, with extremes of 4 times too low and 37 times too high (Limm et al., 1996).

(2) Worst-case approach

The use of modelling for regulatory purposes requires that predictions are always on the safe side. It is not acceptable that a packaging material could be approved by a model prediction, while it would have been rejected by a migration experiment. A significant contribution in this area has been given by Piringer and colleagues (Piringer, 1994, Baner, Brandsch, Franz, Mercea & Piringer, 1995, Baner, Brandsch, Franz & Piringer, 1996, Brandsch, Mercea & Piringer, 2000, Piringer et al., 2000) who have developed a model to predict migration values that are always higher than experimental values, a so-called ‘worst-case’ approach. For this purpose they collected hundreds of measured diffusion coefficients and results of migration experiments reported in literature (Mercea, 2000, European Thematic Network, 2001). They proposed the following equation:

$$D = 10^4 \exp\left(A_P' - 0.1351 M^{\frac{2}{3}} + 0.003 M - \frac{C + 10454}{T} \right) \tag{2.3}$$

where A_P' and C are polymer specific parameters. The equation is adapted to different polymer types by changing A_P', which has been determined for a large number of polymer types including polyethylene, polypropylene, polyesters and polyamides. A_P' was determined either directly from diffusion coefficient values, or indirectly from migration values. To account for temperature effects in polymers, C is set to 0 or 1577 depending on the polymer type (Piringer et al., 2000).

(3) Stochastic approach

In contrast to the worst-case approach, a stochastic approach not only provides a diffusion coefficient, but also information on the certainty of the predicted value. This enables the calculation of the probability that a given migration limit is exceeded. The background of this approach is treated elsewhere (Helmroth et al., submitted) and is only briefly discussed here. For calculating a mean diffusion coefficient, the following equation was proposed:

$$D = a \exp\left(-\left(\frac{M}{M_0} \right)^b \right) \qquad (2.4)$$

where M is the molar mass (g mol^{-1}), M_0 is a reference value of 1 g mol^{-1} and a and b are parameters specific for each polymer and temperature. Parameters a and b and the probability distribution of the diffusion coefficient were derived from a data-set of experimental diffusion coefficient values in polyolefins at nominally 23°C (European Thematic Network, 2001).

Comparison of approaches

The different equations have been compared in Figure 2.3a-c with experimental data[1] for polyolefins at nominally 23°C (European Thematic Network, 2001). Any equation gives a reasonable, but rough, estimation of the diffusion coefficient. The deterministic equation (2.2) gives too low diffusivities in MDPE and HDPE. The ‘worst case’ equation (2.3) indeed overestimates nearly all data. The dotted lines show the approximate 95%-confidence intervals of the prediction of the diffusion coefficient by equation (2.4). It can be concluded that predictions using equation (2.2) and (2.3) in most cases lie within this interval. The range of experimental diffusion coefficients is wide (in some cases even four orders of magnitude!).

2.6 Partition coefficient

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[1] Note that the diffusion coefficient is here reported using units cm^2 s^{-1}.

There are only a few reports on the prediction of partition coefficients, although the distribution of migrant between packaging and food simulant is just as important as the diffusion rate. Experimental research on partition coefficients has been carried out by Kinigakis, Miltz and Gilbert (1987), Gavara, Hernandez and Giacin (1996), Pushpa, Goonetilleke and Billingham (1996) and Hernandez-Muñoz, Catalá and Gavara (2001). Theories have been given to predict the solubility of small compounds in polymers (Krevelen, 1990, Bicerano, 1996). However, these are not sufficiently accurate for predicting the solubility of monomers and additives. A rough estimation of the partition coefficient, defined as the ratio of concentration in packaging to concentration in food simulant, is given by Baner et al. (1996). Based on experimental migration results, he proposes a value of 1 for migrants with a high solubility in the food simulant and 1000 for those with a poor solubility.

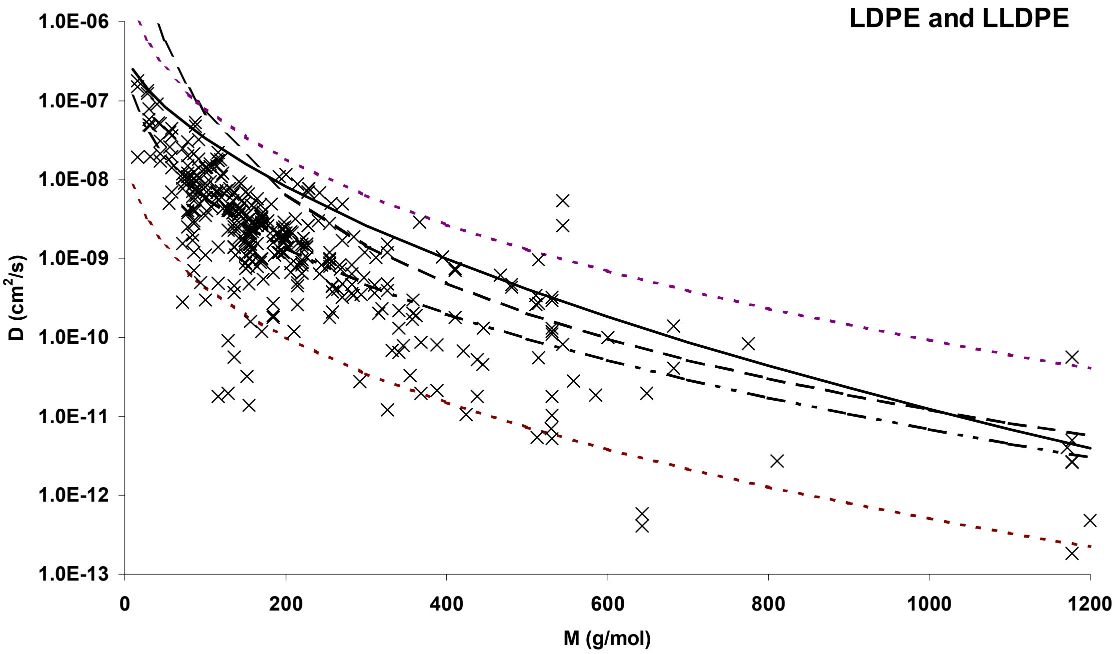
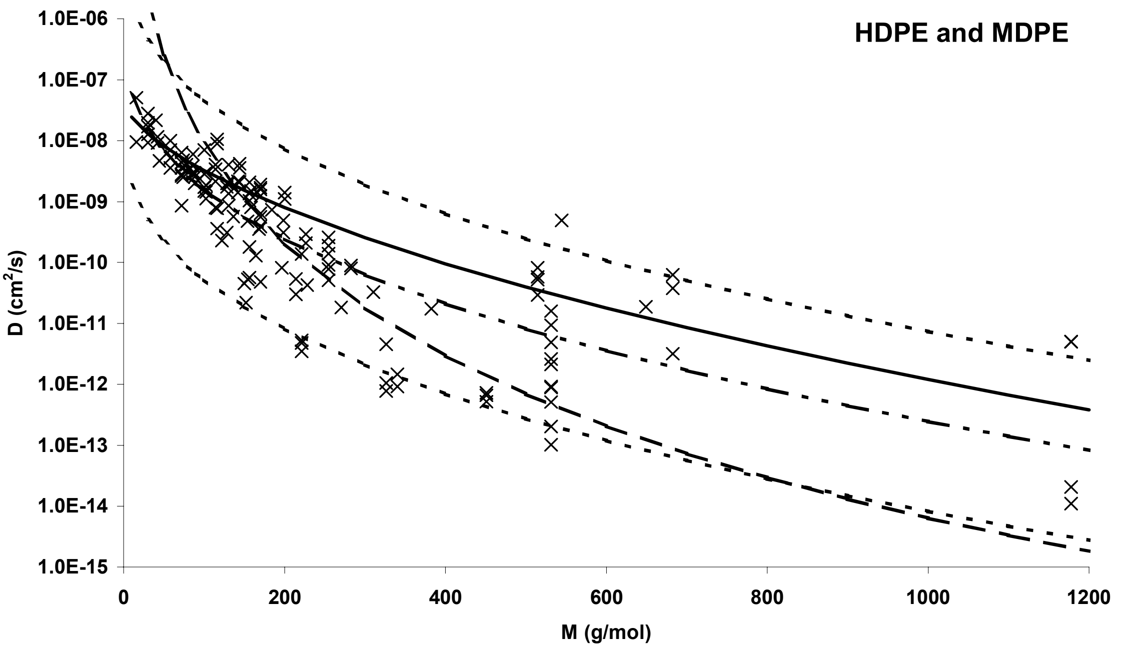


Figure 2.3a Comparison of different models for predicting the diffusion coefficient as a function of migrant molar mass in LDPE and LLDPE with experimental data (European Thematic Network, 2001). Experimental data shown as '×', deterministic approach (eq. 2.2) as '---', worst-case approach (eq. 2.3) as '—', and stochastic approach (eq. 2.4) as '-···-' with '.....' as approximate 95% confidence interval.



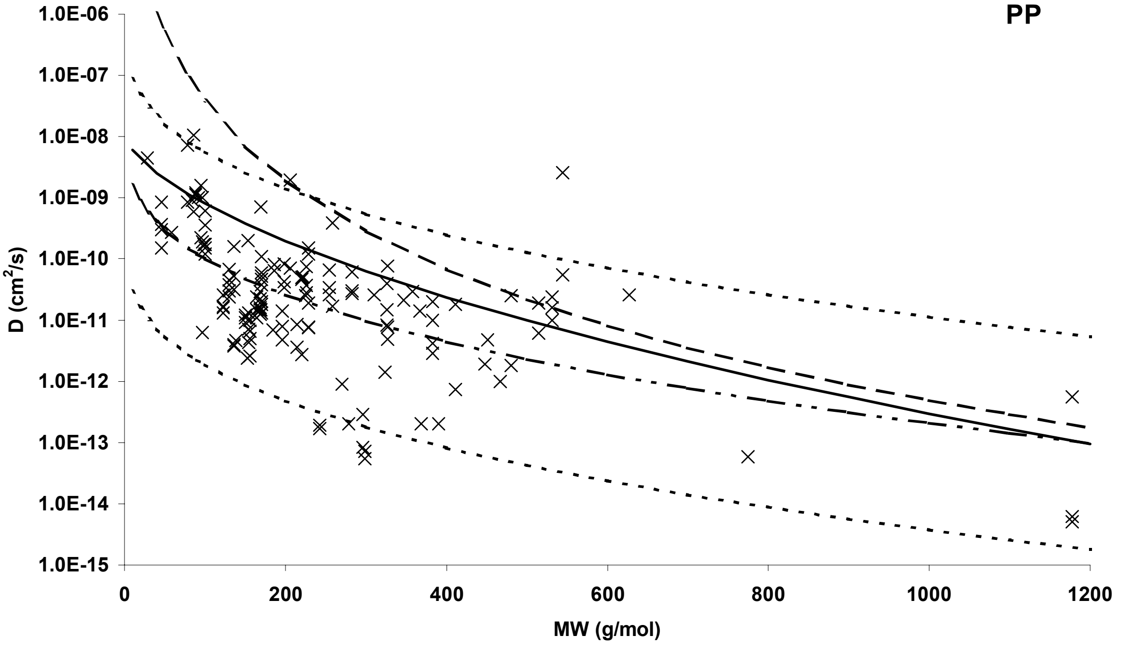


Figure 2.3b,c Comparison of different models for predicting the diffusion coefficient as a function of migrant molar mass in MDPE and HDPE (upper figure) and PP (lower figure) with experimental data (European Thematic Network, 2001). Experimental data shown as '×', deterministic approach (eq. 2.2) as '---', worst-case approach (eq. 2.3) as '—', and stochastic approach (eq. 2.4) as '-···-' with '·····' as approximate 95% confidence interval.

2.7 Application for regulatory purposes

To show that packaging materials comply with regulations, we can either use predictions or experiments. It is vital that predictions do not lead to approval of a material that would be rejected by experiment. Adding a high safety factor to the prediction may prevent this. However, if a model gives too many false positives, then the usefulness of the model decreases since experiments have to be carried out anyway. There are rapid developments in packaging technology aiming for better product quality and waste reduction, so there is a need for more rapid test methods at an early stage in the development process in demonstrating compliance of commercial products. Model predictions can be useful in this respect if they provide realistic values.

The results in Figure 2.3 give an impression of how good the different diffusion coefficient models are. Considering the partition coefficient, the proposed value of 1 for migrants with high solubility in the simulant seems realistic. For compounds with a poor solubility, the value of 1000 may lead to excessive overestimation of experimental migration values since the value may be much higher. However, predictions using this value are usually on the safe side. If it would turn out that predictions too often incorrectly exceed migration limits, then refinement of this value may be required.

Since migration is the result of both diffusion and partitioning, model validation should also be carried out with real migration values. To our knowledge, no reports have been published on the validation of the deterministic approach by Limm et al. (1996). With the stochastic approach, the most likely migration values from a given packaging/food combination can be calculated. Validation of this approach is not yet possible because insufficient migration experiments have been performed for one particular molar mass (but with different compounds) under standard conditions.

The ‘worst-case’ approach of Piringer and colleagues has had a lot of attention in the discussion on migration modelling for regulation in Europe. Results obtained by O’Brien, Goodson and Cooper (1999) and O’Brien and Cooper (2001) show that most of the migration values of four different additives from HDPE and PP are indeed overestimated by this model. In a recently finished European thematic network (2001), a large amount of migration data was collected and values for A_P' and C were determined. The result of this project was a document on how to apply migration predictions based on this ‘worst-case’ approach as an alternative test method in European packaging legislation.

The model is indeed useful for getting rough estimates of the migration rate of polymeric compounds. However, although the model has been shown to give good results for polyolefins at ambient temperatures, it should be used with care at higher temperatures, higher molar masses and for non-polyolefins until more experimental data are available. For instance, if predicted diffusion coefficient values at 70°C in PP are compared with experimental values measured by Reynier et al. (2001), more than 50% of the 23 experimental values are higher than the predicted values.

We think that stochastic modelling is useful for obtaining realistic predictions. For extended application, more knowledge is needed on both diffusion and partition coefficients, in different materials and under different conditions.

2.8 Conclusions

Predicting migration is a promising cost- and timesaving alternative to migration experiments. The use of stochastic models has the advantage of giving a realistic prediction in combination with a probability distribution, which enables a better risk evaluation. However, the use of any migration model must be accompanied by knowledge on the background and application area of the model. Further research is needed to improve current models, both by fundamental research on diffusion in polymers and by well-considered applied research on real packaging and food or food simulant combinations.

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3

Predicting migration from polyolefins using stochastic modelling[2]

Abstract

A method is presented to predict diffusion coefficients in polyolefins using stochastic modelling. A large number of experimental diffusion coefficients, published in literature as one data-set, was used to derive probability distributions of diffusion coefficients in the polymers LDPE and LLDPE, MDPE and HDPE, and PP. An equation is proposed to describe the diffusion coefficient as a function of the molar mass of the migrant. Model parameters and standard deviations are predicted by minimizing the sum of squared errors and the residuals are used to check the assumed types of probability distribution. The experimental data can be described by a log-normal distribution. It is shown how the derived probability distributions can be used as input for migration predictions. The method presented provides information about the most likely migration results for a given packaging/food simulant combination. This is important for prediction of the probability that a given migration limit may be exceeded.

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[1] submitted by I.E. Helmroth and C. Varekamp

3.1 Introduction

Research during the second half of the 19th and first half of the 20th century, as reviewed by Crank and Park (1968), shows that the transport of small molecules through polymers can be described as a diffusion process. This was later shown also to be the case for migration of larger molecules (such as monomers and additives) from plastic packaging materials to foods or food simulants (Moisan 1980, Reid 1980, Figge and Hilpert 1990a, 1990b). By using an appropriate diffusion model, it is possible to predict migration as a function of time. Such models are useful for predicting exposure risks of toxic compounds in packaging materials and may in some cases replace time-consuming and expensive migration experiments currently required for demonstrating compliance with food packaging regulations. The key question, however, is how to obtain values for the model parameters that are characteristic of each combination of migrant, packaging material and food simulant. *A priori* prediction from physical properties alone is impossible, since the precise factors determining migration are not known. The use of semi-empirical relationships derived from experimental data is therefore inevitable.

A relatively simple migration model is given by a solution of Fick diffusion equations containing two model parameters: a diffusion coefficient (D) and a partition coefficient (K). The diffusion coefficient represents the migration rate in the polymer and the partition coefficient represents the distribution of migrant over packaging and food simulant at equilibrium. Empirical relations for the diffusion coefficient as a function of the molar mass of the migrant and temperature have been proposed (Limm and Hollifield 1996, Piringer and Baner 2000). The latter used a 'worst-case' approach based on a large number of experimental diffusion coefficients found in literature. This equation has been shown to overestimate migration from polyolefins in most cases (O'Brien and Cooper 1999, O'Brien *et al.* 2001). However, the disadvantage of a 'worst-case' approach is that no information is obtained about the uncertainty of the prediction. Using the large number of experimental data available, stochastic modelling can be applied to determine probability distributions, i.e. curves that show the probability of finding a given diffusion coefficient. From the probability distribution of the diffusion coefficient (and if available the partition coefficient), the probability of exceeding a certain migration limit can be calculated. Probability distributions of migration are also needed as input in stochastic models that predict exposure from food packaging based on the concentration of a toxic compound in the food, food consumption and absorption by the body (Petersen 2000).

The goals of this paper are to show (1) how probability distributions can be derived for diffusion coefficients of migrants in polyolefins, and (2) how these distributions can be used for migration prediction.

3.2 Theory

Migration of a compound from plastic to a contacting food simulant is often calculated as a function of time by solution of the second diffusion equation of Fick. This analytical solution is given by (Crank 1975)

$$\frac{M_{F,t}}{M_{P,0}} = \left(\frac{\alpha}{1+\alpha}\right)\left[1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp\left(-Dt\frac{q_n^2}{L^2}\right)\right] \tag{3.1}$$

where $M_{F,t}$ is the migrant mass in the food simulant (kg) after time t (s), $M_{P,0}$ the initial migrant mass in the polymer (kg), D the diffusion coefficient ($m^2 \ s^{-1}$), L the polymer thickness (m), $\alpha = V_S/(V_P \cdot K)$ (-), V_P and V_S are the volumes of plastic and food (m^3), $K = C_P/C_F$ (-) is the partition coefficient, C_P and C_F are the migrant concentrations in the plastic and food at equilibrium ($kg \ m^{-3}$) and q_n are the non-zero, positive roots of equation $\tan(\alpha) = -q_n\alpha$ where n is an index variable.

Equation (3.1) assumes that (1) the migrant is homogeneously distributed in the polymer, (2) there is no mass transfer resistance at the interface between polymer and solvent, (3) there is no diffusion from the polymer surface that is not in contact with the food simulant, (4) the food simulant is well mixed, and (5) the polymer matrix does not change (no swelling).

3.3 Experimental data

In this study, we used the diffusion coefficient values at 23°C collected from literature by Mercea (2000)[1] for the groups of polymer types LDPE (low density polyethylene) and LLDPE (linear low density polyethylene), MDPE (medium density polyethylene) and HDPE (high density polyethylene), and PP (polypropylene). The diffusion coefficient values were measured by a number of different researchers during the past four decades using different measurement methods. They were either measured directly at 23°C or they were extrapolated by Mercea (2000) to 23°C from other temperatures.

3.4 Diffusion coefficients and molar mass

The first step was to find a relationship between the diffusion coefficient and properties of additive and polymer. A polymer matrix can be regarded as a network of polymer molecules containing holes with different size and shape. The diffusion rate in this matrix depends on the size and shape of the migrants and on the size and shape of the holes. The smaller the molecule, the higher the chance of finding a hole that is large enough for passing and thus the higher the diffusion coefficient (Brydson 1995). Similarly, the smaller and less frequent the holes, the smaller the diffusion coefficient. According to the free-volume theory of diffusion (Cohen and Turnbull 1959), the diffusion rate of a migrant is proportional to the probability of finding a neighbouring hole with a volume equal to or larger than the volume of the migrating molecule. This probability is a negative exponential function of the molecular volume of the migrant and the available space (Duda and Zielinski 1996). An exponential dependency of the diffusion coefficient as a function of molecular diameter or volume has been confirmed by direct measurements (Berens and Hopfenburg 1982, Reynier *et al.* 2001). In migration predictions the volume is often replaced by the molar mass for simplicity (Piringer 1994, Limm and Hollifield 1996, Reynier *et al.* 2001).

The free-volume theory motivated us to assume the following semi-empirical relationship between the diffusion coefficient and molar mass:

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[1] Note that in this chapter the diffusion coefficient is reported in units of $cm^2\ s^{-1}$ since the literature data were also in these units.

$$D = a \exp\left(-\left(\frac{M}{M_0}\right)^b\right) \tag{3.2}$$

where M is the molar mass (g mol^{-1}), M_0 is a reference value of 1 g mol^{-1} and a and b are model parameters. This expression resembles the free volume equation (Duda and Zielinski 1996, p. 145). However, an extra parameter b was introduced since this improves the fit with the experimental data. Because the hole frequency in the polymer matrix depends on polymer properties such as density and crystallinity, a and b differ for different polymers.

3.5 Stochastic model

In any set of experimental data there will be a distribution around a mean. In this case, differences between experimental diffusion coefficient values and the mean diffusion coefficient as calculated by equation (3.2) depend on two types of errors. The first type is experimental measurement error and variation in experimental set-up (method, temperature, etc.). The second type is caused by physical variation due to small differences in the properties of additive, polymer and food simulant, such as in polarity, density, crystallinity and shape. The approach in stochastic modelling is to assume that the diffusion coefficient is a random variable with a given probability distribution. Assuming that this is a normal distribution, parameters a and b of equation (3.2) were estimated from the experimental data for LDPE and LLDPE by minimizing the sum of squared errors given by

$$SS = \sum_{i=1}^{N} \left(D_{\mathrm{exp},i} - D_{\mathrm{pred},i}\right)^2 \tag{3.3}$$

where N is the number of experimental data. A Simplex iteration method was used for the minimization procedure (Press *et al.* 1994). The smallest SS was found for a equal to 2.0×10^{-6} and b equal to 0.36. With these values equation (3.2) is plotted in figure 3.1a together with the experimental data. Figure 3.1b shows that the residuals, calculated as the difference between experimental and predicted diffusion coefficients,

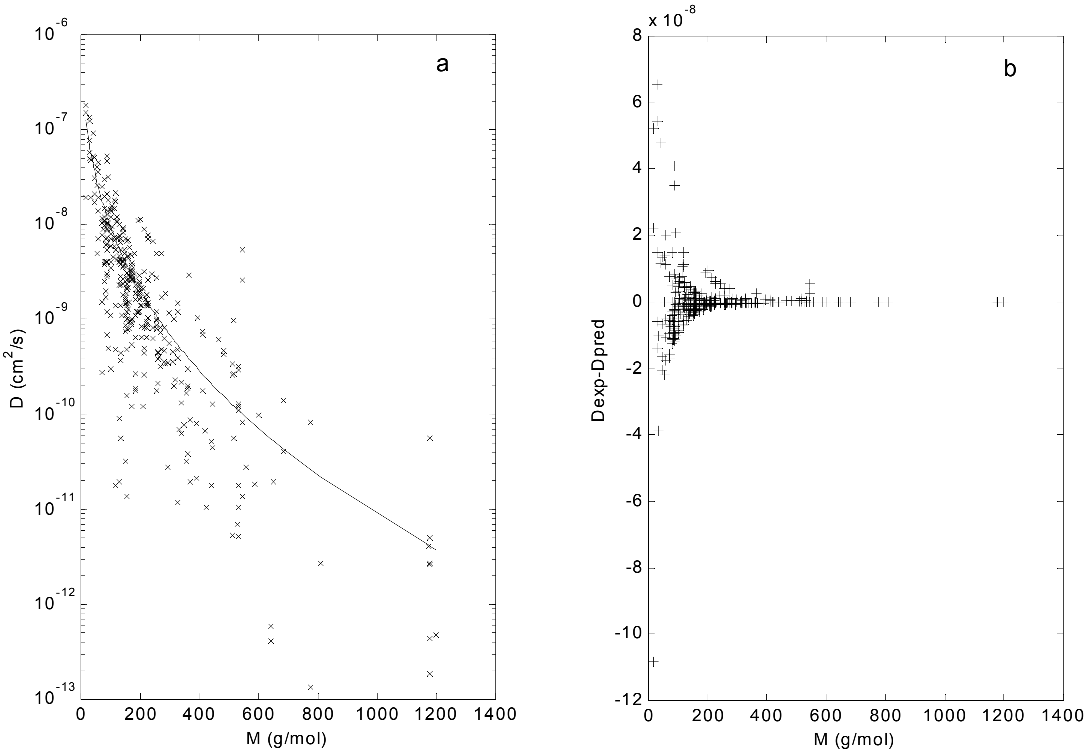

Figure 3.1 Result of minimization procedure of diffusion coefficient with experimental data for polymer group LDPE and LLDPE assuming a normal distribution of errors: (a) experimental data shown by '×' and best fit by a solid line, (b) residuals.

depend on the molar mass of the migrant. The residuals are larger for smaller than for larger migrants.

Taking the natural logarithm of the diffusion coefficient values makes the residuals approximately independent of molar mass (see figure 3.2b). Ln(*D*) is assumed to be normally distributed, from which it follows that the diffusion coefficient itself has a log-normal distribution (Papoulous 1991). Parameters *a* and *b* were determined from the experimental data by minimizing the sum of squared errors now given by

$$SS = \sum_{i=1}^{N} \left(\ln D_{\mathrm{exp},i} - \ln D_{\mathrm{pred},i} \right)^2 . \tag{3.4}$$

The best fit is shown in figure 3.2a together with the experimental data; values of the parameters *a* and *b* are given in table 3.1. Figure 3.2c shows the histogram of the residuals, derived by classification of the residuals by size and counting the number of

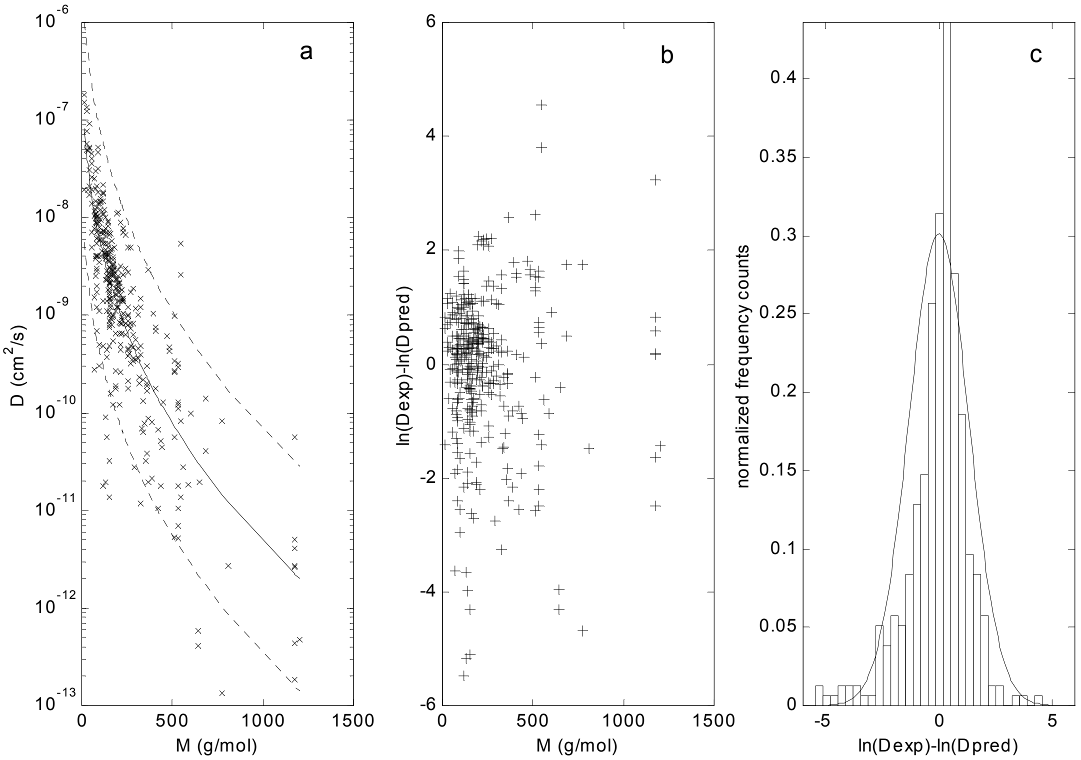

Figure 3.2 Result of minimization procedure of diffusion coefficient for experimental data for LDPE and LLDPE polymers assuming a log-normal distribution of errors: (a) experimental data shown by '×', best fit by a solid line and the 95%-confidence limits (see text) by a dotted line, (b) residuals, and (c) histogram of the residuals (bars) and normal curve with zero mean and σ equal to 1.3 (solid line).

times that the residuals fall within a given bin in a range of bins with defined edges. The histogram was normalized by dividing the frequency counts by the total number of experimental values and by the bin size, to enable comparison with the predicted (normal) probability distribution (shown by a solid line). The histogram shows that the residuals approximately follow a normal distribution. A log-normal distribution therefore seems to be a reasonable assumption.

The standard deviation (σ) is estimated by (Papoulis 1991)

$$s = \sqrt{\frac{1}{N-1}\left[\sum_{i=1}^{N}\left(\ln D_{\exp,i} - \ln D_{\mathrm{pred},i}\right)^2 - \left(\sum_{i=1}^{N}\left(\ln D_{\exp,i} - \ln D_{\mathrm{pred},i}\right)\right)^2\right]} \qquad (3.5)$$

Table 3.1 Estimated model parameters *a* and *b* in equation (3.1) and standard deviation *s* for different groups of polyolefins

Polymer group	*a*	*b*	*s*
LDPE and LLDPE	1.2×10^{-6}	0.37	1.3
MDPE and HDPE	7.2×10^{-7}	0.39	1.6
PP	1.9×10^{-8}	0.36	2.0

and is shown in table 3.1.

95%-confidence limits were approximated by $D_{mean} \pm 2\sigma$ (Miller and Miller 1993) and are shown in figure 3.2a by dotted lines. The probability that a diffusion coefficient lies within the interval defined by these limits is about 95%. In a worst-case approach, the upper limit curve (or a limit given by any other probability value) can be used for the prediction of an upper value of the diffusion coefficient.

For the polymer groups MDPE and HDPE, and PP, probability distribution models were determined in the same way. Figures 3.3 and 3.4 show the results and values for *a*, *b* and *s* are given in table 3.1. Also for these polymer groups, the assumption of a log-normal distribution of the diffusion coefficient is reasonable.

A closer look at the experimental data in figures 3.2a, 3.3a and 3.4a shows that most values of the migrant molar masses lie in the range from 0 to 200 g/mol. This is because most research on diffusion in polymers has been carried out with small molecules. However, most polymer additives have a molar mass between 300 and 1000 g/mol. Equations for estimating diffusion coefficients for migration calculations based on literature data therefore extrapolate to high molar masses. Some additives are used more often for research than others. For example, many data points for a migrant molar mass of 521 g mol^{-1} are available in all polymer groups. This is the antioxidant Irganox 1076, which is frequently used in polyolefins and also in experiments to determine diffusion coefficients. The large variation in the values of this component shows that the experimental method and the conditions of measurement have a large influence on the diffusion coefficient.

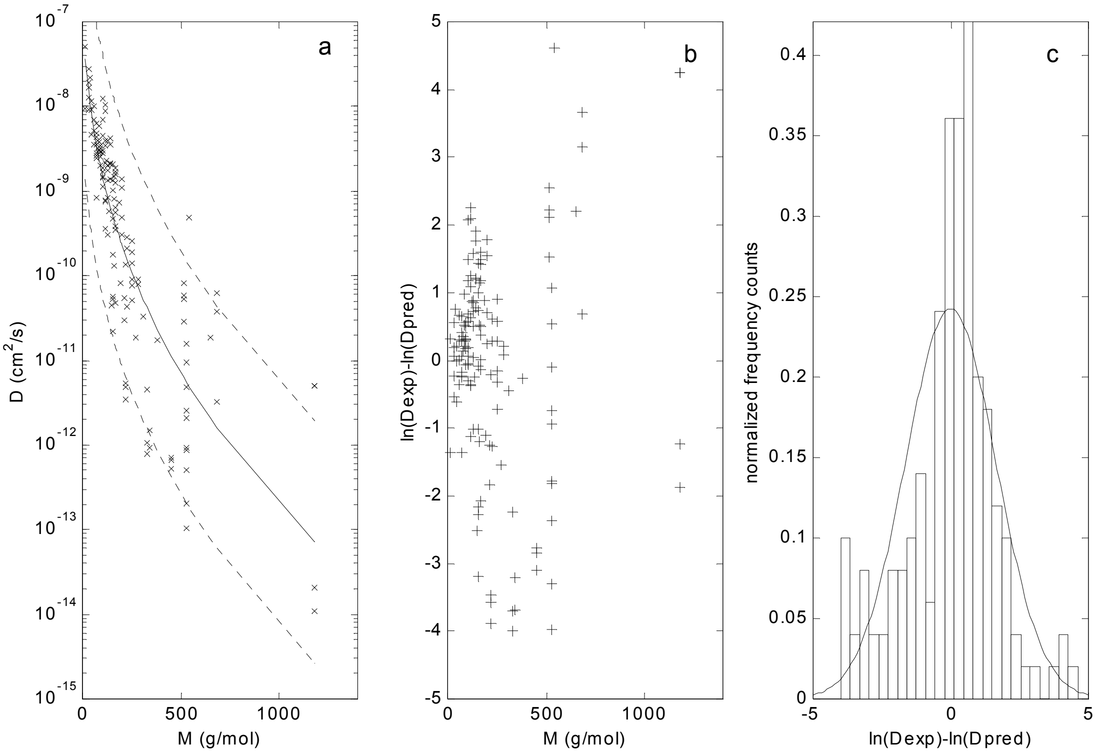

Figure 3.3 Result of the minimization procedure of diffusion coefficient for experimental data for polymer group HDPE and MDPE assuming a log-normal distribution of errors: (a) experimental data shown by '×', best fit by a solid line and the approximate 95%-confidence limits (see text) by a dotted line, (b) residuals, and (c) histogram of the residuals (bars) and normal curve with zero mean and σ equal to 1.6 (solid line).

3.6 Migration simulations

Finally, the probability distributions of the diffusion coefficients were used for migration prediction. The partition coefficient was assumed for simplicity to have one value with no error. According to Baner *et al.* (1996), the partition coefficient, defined as the ratio of concentration in packaging to concentration in food simulant, is 1 for migrants with a high solubility in the food simulant and 1000 for a low solubility.

To obtain migration probability distributions we used a Monte-Carlo procedure with the following steps:

(1) Select a molar mass of the migrant

(2) Calculate the mean diffusion coefficient using equation (3.2) and corresponding

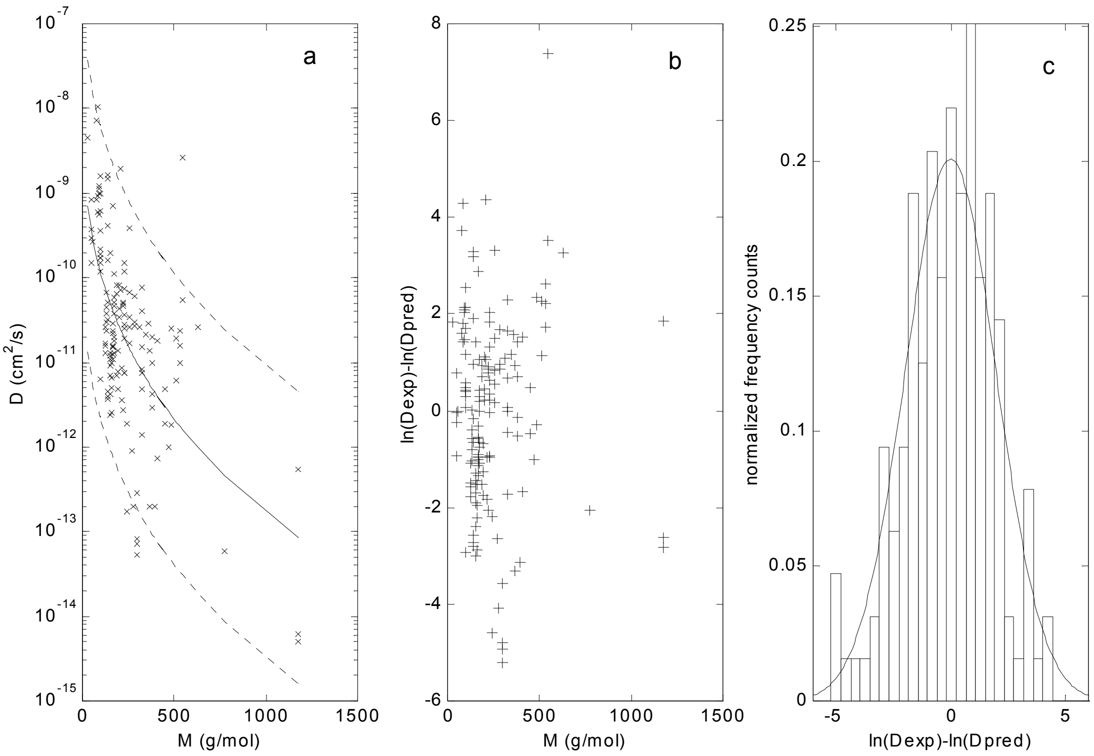

Figure 3.4 Result of the minimization procedure of diffusion coefficient for experimental data for polymer group PP assuming a log-normal distribution of errors: (a) experimental data shown by '×', best fit by a solid line and the approximate 95%-confidence limits (see text) by a dotted line, (b) residuals, and (c) histogram of the residuals (bars) and normal curve with zero mean and σ equal to 2.0 (solid line).

parameter values for *a* and *b* from table 3.1.

(3) Draw a random diffusion coefficient from the probability distribution given by the mean diffusion coefficient and *s* using

$$\ln D = \ln D_{mean} + sR \tag{3.6}$$

where *R* is a random number from a normal distribution with zero mean and standard deviation equal to 1.

(4) Calculate the migration by using equation (3.1)

(5) Repeat steps 3 and 4 a large number of times (here 10,000 times)

(6) Plot a histogram of the obtained migration values.

To illustrate the method, the migration of Ultranox 640 (PM/REF 95270) with a molar mass of 450 g mol^{-1} from a 200 µm thick PP polymer film at 23°C is calculated. The initial additive concentration is assumed to be 500 mg kg^{-1} and the dimensions of a standard EC packaging (6 dm^{2} contact area/ kg food) are used. Polymer density is assumed to be 0.95 kg dm^{-3} and food simulant density 1 kg dm^{-3}. The specific migration limit of Ultranox 640, according to EC Directive 90/128/EEC and its amendments (Commission Directive 2001/62/EC 2001), is 2 mg kg^{-1} food. Test conditions are officially 10 days at 40°C, but since our model is only applicable at 23°C, we arbitrarily assumed test conditions of 20 days at 23°C.

Figure 3.5 shows the results of the Monte-Carlo procedure for a fatty food simulant (K = 1). The distribution of migration values is broad, which means that both low and high migration values are possible. This is due to the large variation in the experimental diffusion coefficients (included in the standard variation). According to the results, it is most likely to find a migration value in the range of 0 to 1 mg kg^{-1}. However, higher migration values are possible. The shape of the curve results from the log-normal distribution of the diffusion coefficient. If the partition coefficient in equation (3.1) would also be provided with a probability distribution, then another distribution of migration values may be found. The peak at 5.9 mg kg^{-1} is due to the fact that the maximal concentration in the food simulant (according to the thermodynamic equilibrium) has already been reached for all of the highest diffusion coefficient values.

The cumulative of the frequencies shown in figure 3.5 gives the probability of finding a migration value less than or equal to a given limit (figure 3.6). In our example, the probability that the migration is less than or equal to 2 mg kg^{-1} is 0.86, which corresponds with a chance of 0.14 of exceeding this limit.

In principle, the estimated parameters *a* and *b* also have an uncertainty, which may be included in the predictions by introducing a probability distribution for each parameter as well. A method to include uncertainty in the parameters is given on page 689 in Press *et al.* (1994).

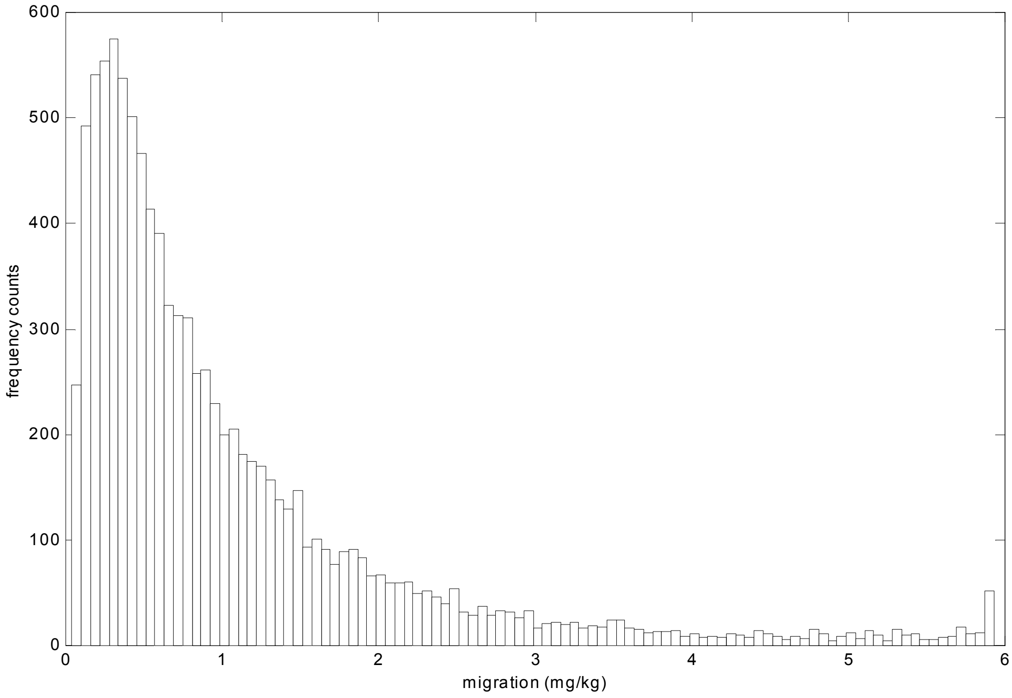

Figure 3.5 Probability distribution of the migration of Ultranox 640 from a PP polymer film at 23°C during 20 days of incubation (see text for further details).

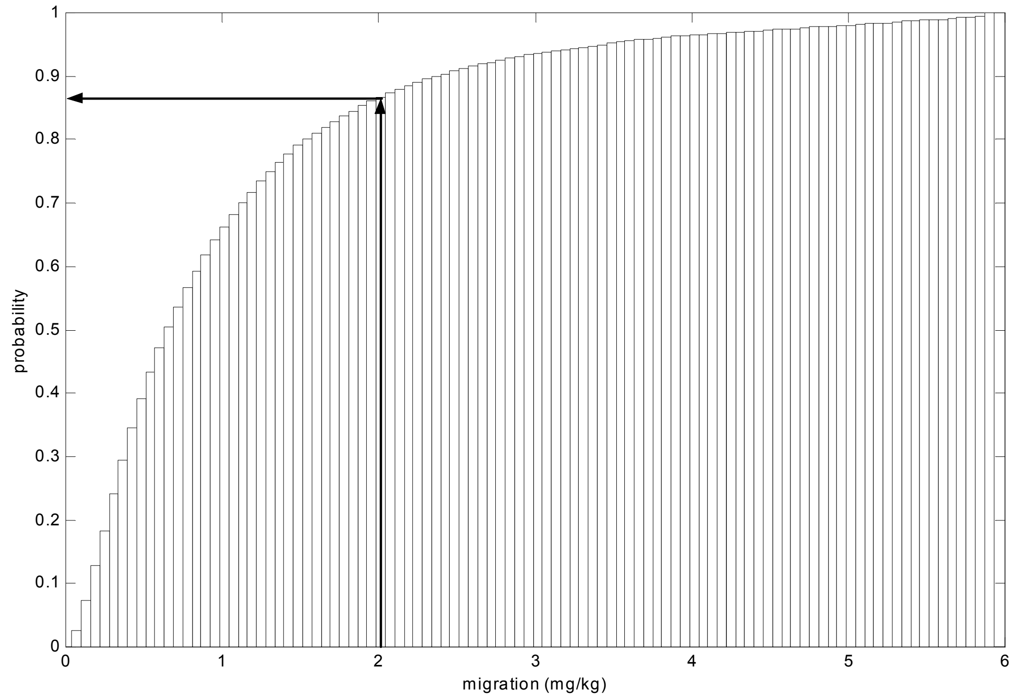

Figure 3.6 Probability of finding a migration value less than or equal to the migration value given on the *x*-axis for the migration situation described in the text and shown in figure 3.5. The arrows indicate the probability of finding a migration value less than 2 mg ml^{-1}.

3.7 Discussion

The derived probability distributions are for a temperature of 23°C. To include other temperatures, there are two options. The first is to collect diffusion coefficients at another temperature, for example 40°C, and again derive the parameters a and b and standard deviation s. The other is to include a temperature dependency in equation (3.2) or using another expression for the diffusion coefficient as a function of temperature. However, this requires many experimental diffusion coefficient values of different migrants at different temperatures. Sufficient values have yet not been measured, especially at higher temperatures and for higher molar masses, to allow this type of stochastic approach.

The choice of a type of distribution is the most important and difficult part of stochastic modelling, since this determines the probability of a given diffusion coefficient. The log-normal distribution gives a reasonable, although not perfect, fit of the experimental data. It is important to remember that the diffusion coefficients have been determined by many different methods and under very different conditions. Since the available data are rather noisy, it does not seem worthwhile to apply more complex distributions, or even different distributions for each polymer group, until this is justified by more experimental data.

3.8 Conclusions

The purpose of this paper has been to show how stochastic modelling can be applied to derive probability distributions of diffusion coefficients of migrants in polyolefins based on results of diffusion experiments reported in literature. The probability distributions can be used to simulate migration processes and predict the probability of exceeding a given migration limit. The model presented can be used for migration prediction in polyolefins at 23°C. More experimental data may allow extension to other temperatures and to a more justified choice of type of probability distribution.

Acknowledgements

The authors wish to thank Professor Tiny van Boekel (Wageningen University) for critically reading the manuscript.

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Influence of solvent absorption on migration from LDPE[1]

Abstract

This study is on the simultaneous diffusion of a migrant (Irganox 1076) and a solvent in low density polyethylene (LDPE). The migrant diffuses out of the polymer while the solvent is diffusing inwards. The influence was tested of different solvents: ethanol, isopropanol, isooctane, ethylacetate, cyclohexane, tributyrin, tricaprylin and olive oil. The concentration of Irganox 1076 in the liquid outside the polymer was measured as a function of time. From this curve a diffusion coefficient and a partition coefficient were obtained using the Fick diffusion equation. The equilibrium uptake of solvent by the polymer was measured separately. For solvents with low molar mass the diffusion coefficient of Irganox 1076 increases with increasing solvent uptake. For the two tri-glycerides and olive oil no increase of the diffusion coefficient was found upon solvent absorption (only 1-2%) by the polymer. The result can be used in a new model for the diffusion of migrants in polymers. In this model, the diffusivity depends on migrant and polymer properties, but also on the solvent absorption in the polymer.

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[1] published as 'Influence of solvent absorption on the migration of Irganox 1076 from LDPE', E. Helmroth, M. Dekker and Th. Hankemeier, *Food Additives and Contaminants*, 2002, **19**, 176-183.

4.1 Introduction

Predicting migration of additives and other components with low molar mass from plastic packaging materials to food simulants using mathematical models is a subject of increasing interest. Model predictions may in some cases replace time-consuming and expensive migration experiments which are necessary to test new packaging concepts. Also, mathematical migration models may be used to quantify the effectiveness of a functional barrier layer between a non-food grade layer and a food product.

The transport of components in a polymer is usually described by Fick's law of diffusion (Crank 1975). Given a diffusion coefficient D and a partition coefficient K, migration of a component from a polymer to a solvent can be calculated as a function of time. Both D and K are *macroscopic* parameters, which describe the combined properties of migrant, polymer and contacting solvent at a certain temperature. Empirical relationships of D as a function of molar mass of the additive, polymer type and temperature have been established (Piringer 1994, Limm and Hollifield 1996). However, also properties of the contacting solvent can influence the migration rate. For instance, Koszinowski (1986) and Piergiovanni *et al.* (1999) have shown that components permeating through different polyolefins move faster when the polymer film is in contact with an apolar than with a polar solvent. The last author also found that the diffusion rate of (apolar) isooctane is significantly higher than that of (polar) ethanol in low density polyethylene (LDPE), implying that isooctane migration enhanced the migration rate of the other components. Similarly, the migration rate of small molecules in poly(vinylchloride) (PVC) film was shown to be governed by penetration of the contacting solvent tertiary butyl acetate (Riquet and Feigenbaum 1997). Diffusion depends not only on polarity, but also on molecular size and shape. For instance, the polarity of larger triglycerides is almost equivalent to that of polyolefins, but results in literature do not show an increase in migration by triglycerides. For example, Goydan (1990) found that the migration rates of both Irganox 1076 (octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl propionate)) and Irganox 1010 (tetrakis (methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate)methane) from polyolefins to 95% ethanol were similar to the migration rates to corn oil. Also, O'Brien *et al.* (1999) showed that migration of Irganox 1076 and DEHA (di(2-ethylhexyl)adipate) from polyolefins to 95% ethanol were in good agreement with those to olive oil. In contrast with this, Reynier *et al.* (1999) recently suggested using a D that depends on the local solvent concentration to compensate for the effect on additive migration caused by penetrating solvents, including olive oil and other triglycerides. So the exact role of triglycerides on additive migration is not clear.

According to the free-volume theory, diffusion in polymers occurs by jumping of small molecules through holes available between the twined polymer chains. The presence of the small molecules in the holes results in a larger total free volume, since the small molecules carry a larger free volume than the polymer. This extra free volume allows easier segmental motion of the polymer chains. As a consequence, the diffusion of the components becomes faster as their local concentration increases. This effect is called plasticization and is similar to the effect caused by increasing the temperature (Crank 1968, Hansen 2000, Wesselingh and Krishna 2000). A rule of thumb reported for elastomers is that the solvent diffusion coefficient increases by a factor of about 10 for an increase in solvent concentration of about 15 vol% (Hansen 2000).

The present paper focuses on the effect of solvent absorption by the polymer on migration of additives. The diffusivity, D of Irganox 1076 is related to the maximum solvent absorption in LDPE film. Solvents are selected to cover a broad range of polarities and molecular sizes, including fatty food simulants as used in EC legislation. This results in five organic solvents of low molar mass and varying polarity, two triglycerides and olive oil.

Theory

An analytical solution of the Fick equation for one-dimensional diffusion and limited volumes of packaging and solvent is given by (Crank 1975: equation 4.37)

$$\frac{M_{\mathrm{S},t}}{M_{\mathrm{P},0}} = \left(\frac{\alpha}{1+\alpha}\right)\left[1-\sum_{n=1}^{\infty}\frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2}\exp\left(-D_{\mathrm{eff}}\,t\,\frac{q_n^2}{L^2}\right)\right] \tag{4.1}$$

where $M_{S,t}$ (kg) is the mass of additive in the solvent after time t (s), $M_{P,0}$ is the initial mass of additive in the polymer (kg), D_{eff} is the effective diffusion coefficient (m^2 s^{-1}), L is polymer thickness (m), $\alpha = V_S/(V_P \cdot K)$ (-), V_S is the volume of the contacting solvent (m^3), V_P is the volume of the polymer (m^3), $K = C_P/C_S$ (-), C_P is the additive concentration in polymer at equilibrium (kg m^{-3}), C_S is the additive concentration in solvent at equilibrium (kg m^{-3}), q_n are the non-zero, positive roots of equation: $tan(\alpha) = -q_n \cdot \alpha$; and n is the index variable.

Equation (4.1) further assumes that (1) the additive is homogeneously distributed in the polymer, (2) there is no mass transfer resistance at the interface between polymer and solvent, (3) there is no diffusion from the polymer surface that is not in contact with the solvent and (4) the polymer matrix does not change throughout the migration process.

Experimental

Materials

LDPE film containing Irganox 1076 (octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl propionate)) and LDPE film without any additives were prepared by DSM, Geleen, the Netherlands. The thicknesses of the film containing Irganox 1076 and the film without additives, determined experimentally with a micrometer screw gauge, were 108 µm (S.D. = 5 µm, n = 24) and 99 µm (S.D. = 5 µm, n = 24), respectively. Stock solutions of Irganox 1076 (Aldrich) and internal standard (hexadecyl-3,5-di-tert-butyl-4-hydroxybenzoate, Aldrich) were prepared in duplicate at a level of 1 mg ml^{-1} in 2-propanol. The second stock solution was used to check the concentration of the first stock solution, from which standards were prepared. Ethanol and isooctane were purchased from Merck, ethyl acetate, 2-propanol, cyclohexane and dichloromethane from Baker. Olive oil (Montolivo) was obtained from a local retailer and fulfilled the requirements of the CEN for migration testing (Comité Européen de Normalisation 1999). The purity of tricaprylin (octanoic acid, 1,2,3-propanetriyl ester) was ≥ 98% (GC) and of tributyrin (butanoic acid, 1,2,3-propanetriyl ester) ≥ 90% (GC). All other solvents were of high purity grade.

Determination of maximum solvent absorption

Pieces of LDPE-film without any additives (5×7 cm) were immersed in solvent for different incubation periods. Before weighing on an analytical balance (Mettler Toledo, ±0.01 mg), the films were wiped with a tissue to remove free solvent. Since volatile solvents absorbed in the polymer will evaporate, the weighing procedure was carried out in pre-weighed glass tubes with a screw-cap. The films immersed in triglycerides were cleaned very shortly in three successive baths of pentane before weighing. Five new films were used for each solvent and contacting time. The weight was followed until no more increase in weight was observed. The maximum absorption was estimated by averaging observations taken after a long contacting time.

Determination of initial additive concentration

Soxhlet extraction was carried out to determine the initial content of Irganox 1076 in the LDPE film. Approximately 1 g cut polymer film was weighed into the extraction thimble and extracted during 7 hours with 250 ml of dichloromethane containing the internal standard. The extract was concentrated by evaporation to ~80 ml and analysed by gas chromatography with flame ionization detection (GC-FID), as described below. The LDPE film contained 3584 mg kg^{-1} Irganox 1076 (SD = 8 mg kg^{-1}, n=3), which, assuming a polymer density of 0.92 kg dm^{-3} (Brydson 1995), corresponds to 3297 mg dm^{-3}.

Migration experiments

A migration cell for single-sided contact was designed to follow the concentration of Irganox 1076 in the solvent as a function of time. The cell was made of stainless steel with a screw cap with a septum for sampling with an injection syringe. The septum in the screw cap (silicone with a PTFE layer) was changed after one to four times of sampling as the solvent vapour caused plasticization of the rubber after being pierced with the injection syringe. Preheated cells were filled with 20 ml solvent, a pre-cut polymer film (contact area 38.5 cm^2) was inserted and the cell was tightened firmly by hand. Turning the cell upside down immediately started the contact period. The cells were incubated under gentle shaking (55 rpm) in a water-bath of 40 (±0.3)°C. Samples of 40 µl were transferred to an autosampler vial with a 100 µl insert and 5 µl internal standard solution was added. The samples were analysed by GC-FID as described below.

The sampling procedure with the triglycerides (tributyrin, tricaprylin and olive oil) was slightly different. Samples of ~40 µl were taken with a Pasteur pipette and put into pre-weighed vials with insert, which were weighed again to obtain the exact sample amount. Internal standard solution (5 µl) was added and the sample diluted with 160 µl acetone to enable analysis by high-performance liquid chromatography (HPLC), as described below.
All curves were measured in duplicate, except for olive oil, which was measured in triplicate.

Analytical methods

The concentration of Irganox 1076 in all solvents of low molar mass was analysed by GC-FID equipped with an on-column injector (GC 8000 Series, Fisons Instruments, Milan, Italy). The column used was a 15 m × 0.25 mm i.d. DB5-MS with a film thickness of 0.1 µm (J&W Scientific). The analytical column was connected by a puss-fit to a 0.5 m × 0.53 mm i.d. retention gap, which was deactivated with a thin film of OV-1701-OH (BGB Analytik). Carrier gas was helium at a constant flow rate of 1.8 ml min^{-1}. Samples of 1 µl were injected on-column into the retention gap by an autosampler. The temperature program of the GC oven was 1°C under the boiling point of the solvent during injection and hold for 1 min after injection. The temperature was then increased to 150°C at 15°C min^{-1} followed by an increase at 10°C min^{-1} to 310°C, at which it was held for 1 min. The FID detector temperature was kept at 315°C.

The analysis of the triglyceride samples was based on a method using HPLC developed by O'Brien *et al*. (1997), in which olive oil is diluted with acetone (1:4) before analysis. Analyses were performed by reversed-phase HPLC using a Waters Alliance 2690 system with LC pump, injector and thermostated LC oven and a Waters

474 fluorescence detector (Waters, Milford, US). Separation was achieved by a 150 mm × 4.6 mm i.d. Xterra RP18 column (particle size, 5 µm; Waters). The LC column was kept at 40°C and the samples in the autosampler at room temperature. Detection was achieved by fluorescence detection (excitation wavelength, 282 nm; emission wavelength, 308 nm). A 10 µl aliquot of the triglyceride–aceton mixture was injected. The mobile phase was initially a linear concentration gradient of water/acetonitrile (2/8 v/v) to water/acetonitrile (1/19 v/v). After 5 minutes, the mobile phase was changed to acetonitrile (100%) and kept for 5 minutes. Next, the mobile phase was changed to tetrahydrofuran (100%) to clean the column. Finally, the column was conditioned by water/acetonitrile (2/8 v/v) for 5 minutes before the next injection.

Estimation of D and K

The model parameters *D* and *K* in equation (4.1) were estimated by using the least-square error criterion (Press 1992), which minimizes the sum of the quadratic differences between experimental and predicted amounts of migrated Irganox 1076. As a measure of fit, the root of the mean square error (RMSE) was calculated as

$$RMSE = \frac{1}{M_{P,0}} \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left((M_{S,t})_{\text{experimental,i}} - (M_{S,t})_{\text{predicted,i}} \right)^2} \qquad (4.2)$$

where *N* is the number of experimental points per migration curve and *i* is the observation number.

Results and discussion

Estimation of D and K

Estimated values of *D* and *K* are given in table 4.1. Differences between the duplicate values are likely to be caused by slight variations of, for example, polymer thickness and local initial concentration and by experimental errors, and are in the same order as found in literature (O’Brien *et al.* 1999, Cooper *et al.* 1998). *K* varies in all cases between 0.3 and 11. These values should only be considered as indicative. Low partition coefficients were expected as Irganox 1076 has a good solubility in all selected solvents. Diffusion coefficients of Irganox 1076 in LDPE at 40°C found in literature, measured without solvent contact by a stack of polymer films pressed against a source containing the additive, were 6.9×10^{-14} m^2 s^{-1} and 1.0×10^{-13} m^2 s^{-1} (Földes 1993, Moisan 1980, respectively). The values found here for ethanol, isopropanol and the triglycerides ($0.7 - 1.4\times10^{-13}$ m^2 s^{-1}) are in good agreement with these values.

Figure 4.1 shows the measured migration curves as the amount of migrated Irganox 1076 in the solvent relative to the initial amount in the polymer as a function of time at 40°C. Only one of the duplicate or triplicate migration curves, corresponding to the first value of each solvent in table 4.1, is shown. Control experiments with separate migration cells that were analysed after each contacting time showed that the sampling procedure used in this study does not introduce significant errors. The solvent removed by sampling, with a total maximum of 3% of the initial volume, was not replaced. Gandek (1986) proved mathematically that the error introduced to a migration process by taking samples without replacing the solvent is smaller than in the case that the solvent is replaced.

A good model of migration should give small differences between predicted values and experimental data. A close look at the data points and best-fitting curves in figure 4.1 shows that for ethanol, isopropanol, tributyrin and tricaprylin the Fick equation fits very well. For isooctane, ethylacetate and cyclohexane, the fit is less perfect. For olive oil, the deviation from the Fick equation is large. This is most likely due to the problem of analysing Irganox 1076 in olive oil, which is a complex mixture of different triglycerides. At the retention times of Irganox 1076 and the internal standard, there were no disturbing peaks and the calibration curve and reproducibility were acceptable. However, although the HPLC column was washed with THF between each sample, baseline problems occurred which disturbed the analyses. As both tributyrin and tricaprylin showed perfect fits with the Fick equation, it seems that analytical variation is indeed the reason for the bad fit.

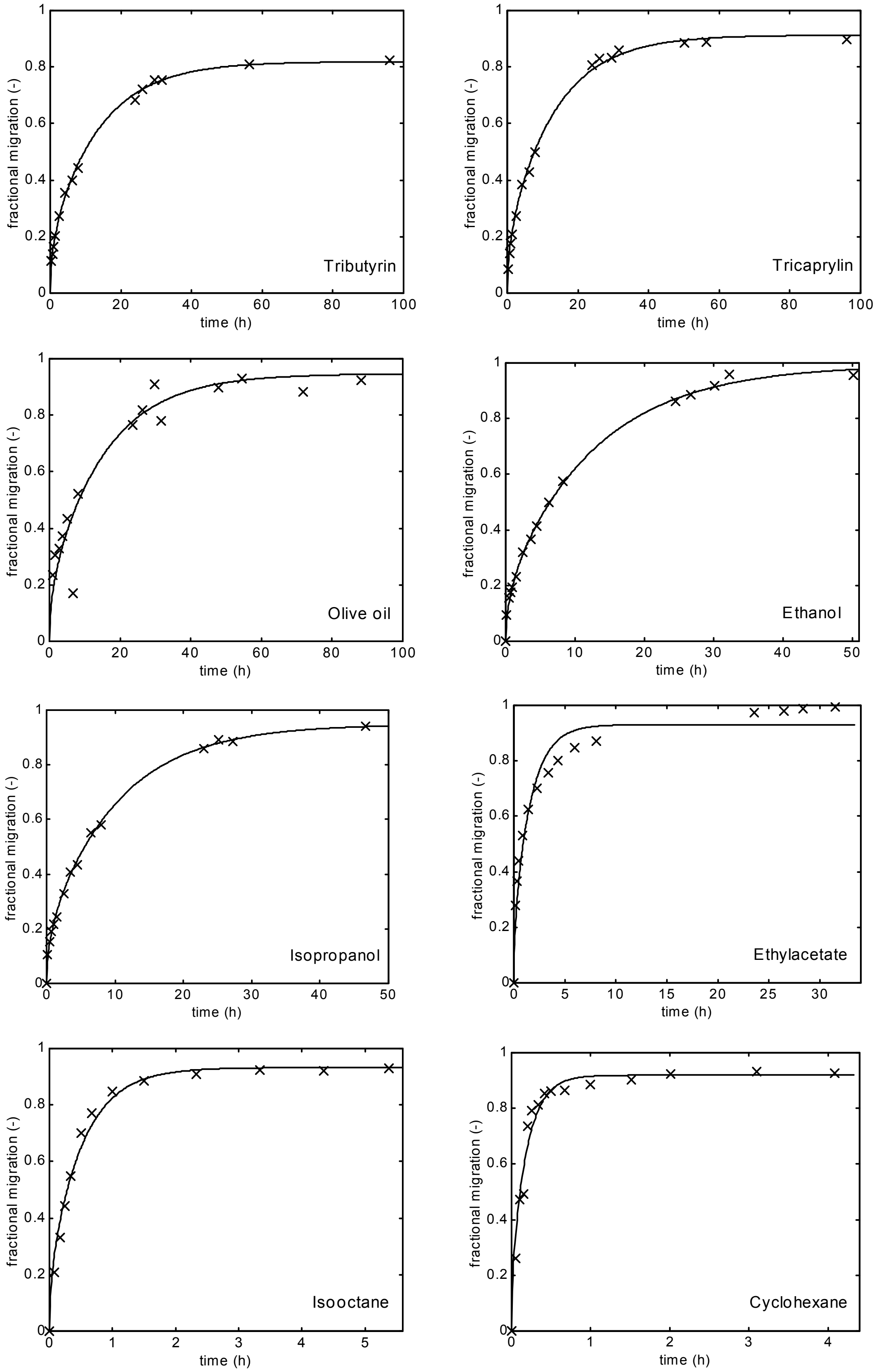

Figure 4.1 Amount of Irganox 1076 migrated from LDPE in the test solvents relative to the initial amount in the polymer as a function of time at 40°C. Experimental data shown as points and best fitting curves as solid lines.

Table 4.1 Effective diffusion coefficients (*D*) and partition coefficients (*K*) of Irganox 1076 migrating from LDPE to the test solvents at 40°C (duplicate or triplicate values).

Solvent	D ($m^2 s^{-1}$) $\times 10^{13}$	K ($m^3 m^{-3}$)
Tributyrin	0.8	11
	0.7	11
Tricaprylin	0.9	5
	0.9	6
Olive oil	0.8	n.d.
	0.9	n.d.
	1.0	n.d.
Ethanol	1.0	0.3
	1.2	3
Isopropanol	1.2	3
	1.4	2
Ethylacetate	7.4	4
	9.3	11
Isooctane	24	4
	27	7
Cyclohexane	64	4
	65	9

n.d., No data.

A quantitative way of determining how well the Fick equation fits, is by calculating the root of mean-square error (RMSE) using equation (4.2). The smaller the RMSE, the better the equation fits the experimental data. The calculated RMSE values in table 4.2 confirm the result observed by eye. Note the large RMSE of the triplicate measurements of olive oil. of the additive.

The migration behaviour of an additive in a solvent can, in accordance with the free-volume theory, be related to the maximum absorption of that solvent in the polymer. When little absorption occurs, the migration behaviour is purely Fickian and *D* is independent of the type of solvent. In contact with isooctane, ethylacetate and cyclohexane, the LDPE is clearly plasticized since considerable solvent absorption occurs which significantly increases *D*. For example, the diffusion coefficient of

Table 4.2 Root of mean square error (RMSE) as a measure of fit of the diffusion equation to the experimental data (duplicate or triplicate values).

Solvent	RMSE
Tributyrin	0.011; 0.025
Tricaprylin	0.016; 0.020
Olive oil	0.087; 0.087; 0.15
Ethanol	0.02; 0.012
Isopropanol	0.010; 0.015
Ethylacetate	0.055; 0.047
Isooctane	0.033 0.028
Cyclohexane	0.045; 0.048

Irganox 1076 increases by a factor of ~25 with a solvent absorption of ~15 vol% (isooctane). This increase is in the same order of magnitude as reported for elastomers by Hanssen (2000).

For the triglycerides, the results do not clearly follow the observed relationship between maximum solvent absorption and *D*. Although the maximum solvent absorption of the triglycerides was slightly higher than that of ethanol and isopropanol, the *D*'s were more or less similar. The low maximum absorption of the three different triglyceride confirms the theory that solvent absorption depends on both polarity and molecular size and shape. Tributyrin and tricaprylin have a low molar mass (M = 302 and 471 g mol^{-1}, respectively) and were therefore expected to have a higher absorption in LDPE than olive oil (M = 800 to 900 g mol^{-1}) and consequently lead to a higher *D* of Irganox 1076. However, this was not the case, which is probably due to the higher polarity of tributyrin and tricaprylin with respect to olive
oil. The fork-like shape of all triglycerides may also be a reason for their low absorption and lack of effect on Irganox 1076. Figge and Rudolph (1979) and Riquet *et al.* (1998) also have shown that tricaprylin and olive oil are to some extent absorbed into polyolefins. However, from the results presented here it can be concluded that the low absorption of all triglycerides has no effect on the migration rate of Irganox 1076 in thin LDPE film.

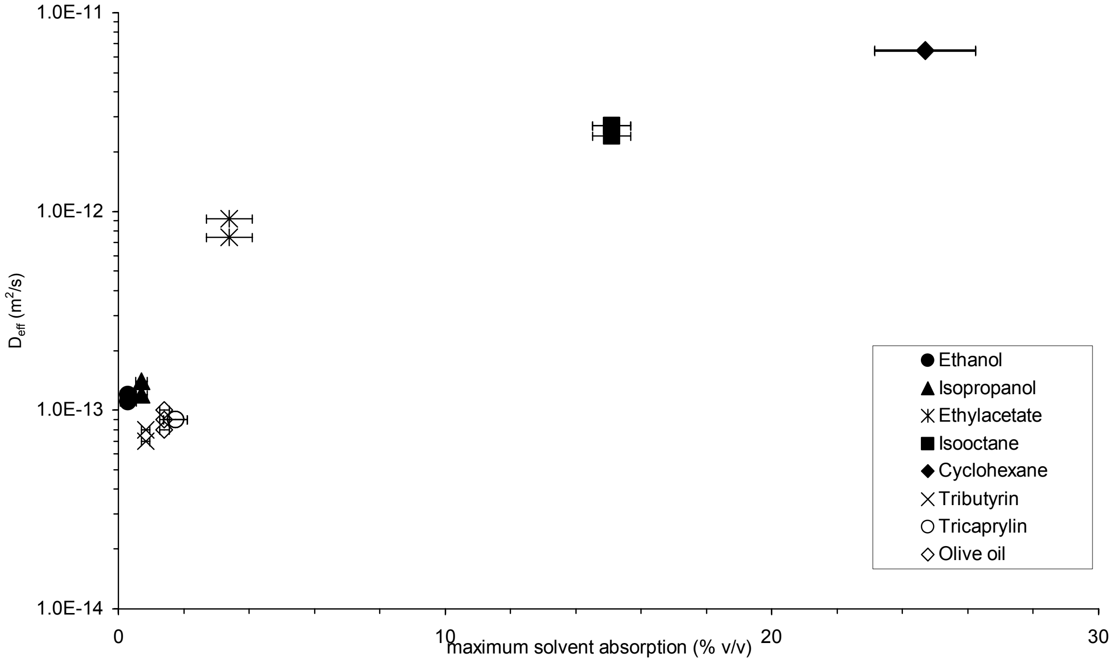

Figure 4.2 Effective diffusion coefficient of Irganox 1076 as a function of maximum solvent absorption. Errorbars are the SD for the determination of solvent absorption obtained for at least 5 measurements at equilibrium.

Conclusion

This study shows that the migration rate of Irganox 1076 from LDPE depends on the type of contacting solvent. It also shows that, for solvents of low molar mass, there is a positive relationship between the migration rate of Irganox 1076 and the maximum absorption of the contacting solvent in LDPE polymer film.

What is the practical value of this result? At the moment, it can be used for prediction of the diffusion coefficient of Irganox 1076 in comparable LDPE films for a certain measured maximum solvent absorption. Further, it is the basis of an extended predictive migration model that is based on the properties of migrant and polymer, and on the absorption of solvent. For such a model, the behaviour of other migrants and polymers with regard to solvent absorption needs to be verified.

In spite of some absorption, none of the triglycerides triggered an increased migration rate compared to the migration rate to solvents that are hardly absorbed in LDPE. The migration behaviour of Irganox 1076 from LDPE film to a triglyceride thus only depends on its own migration rate in LDPE and its solubility in the triglyceride. This result suggests that for LDPE all triglycerides with a molar mass of at least that of tributyrin may be used as an alternative food simulant for olive oil, provided that the solubility of the additive in the triglyceride is good.

Acknowledgements

The authors thank M.A.H. Rijk at TNO Nutrition and Food Research, and Prof. J.A. Wesselingh at the University of Groningen, The Netherlands, for useful discussions, and J. Sampers and J. Hennen at DSM, Geleen, The Netherlands, for providing LDPE film.

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5

Measurement of additive concentration profiles inside LDPE[1]

Abstract

This is a study on the migration of the additive Irganox 1076 from a low density polyethylene (LDPE) slab into ethanol. The local concentrations of the additive were determined for different times as a function of position. This was done by microtoming and GC-analysis. The measured concentration profiles are well described by the Fick diffusion equation with a diffusion coefficient of 1.1×10^{-13} m^2 s^{-1}. This agrees with the value obtained from following the Irganox concentration in the solvent as a function of time. Shaking the ethanol had no effect on the transfer rate, indicating that there is no mass transfer limitation in the solvent. Measurements at different temperatures gave an activation energy for the diffusion coefficient of 113 kJ mol^{-1}.

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[1] accepted as 'Direct measurement of additive migration from low density polyethylene as a function of space and time', I.E. Helmroth, H.A.M. Bekhuis, J.P.H. Linssen and M. Dekker, *Journal of Applied Polymer Science*

5.1 Introduction

The migration of additives from plastics to food or pharmaceuticals is important in packaging technology. In spite of extensive research, there is still a lack of understanding about the migration of large molecules (>200 g mol^{-1}) from a polymer to a contacting solvent. Current migration research depends on the measurement of additive concentration in the contacting solvent. Measurements in the solvent give a direct indication of contamination risk for food products or pharmaceuticals. However, they provide limited information about the migration process, which takes place inside the polymer. The equations used to describe transport of molecules through polymers, are partial differential equations in both time and space and are best studied separately. However, not many papers deal with measurement of local additive concentration in polymers, despite the advantage of obtaining information on the migration as a function of both time and space. Slicing the polymer with a microtome has been shown to give promising results,[1-4] but the method has not been well tested. Besides the study of migration, an evaluation of the method is also important as microtoming may be used to validate new concentration profiling techniques such as confocal microscopy,[5,6] Raman microscopy [7] and NMR [8-10].

The aim of this paper is to validate a method based on microtoming and GC-analysis for studying transport of additives in polymers. As a test case we used a frequently studied combination of the polymer antioxidant Irganox 1076, low density polyethylene (LDPE) and contacting solvent ethanol.[11-14] Validation of the method was performed in two steps:

(1) By checking the mass balance of Irganox 1076 in both polymer and solvent. The total amount of Irganox 1076 in polymer and solvent should always be equal to the initial amount of Irganox 1076 in the polymer.

(2) By comparing the experimental data with the diffusion equations of Fick [15,16] which are known to describe the transport of Irganox 1076 from LDPE to ethanol. [17]

5.2 Theory

Mass balance equation

The mass balance can be written as:

$$M_{\mathrm{p,initial}} = M_{\mathrm{p},t} + M_{\mathrm{s},t} \tag{5.1}$$

where M is the amount (kg) of additive in polymer (p) or solvent (s), initially ($t = 0$) or after contact time t (s).

Diffusion equation

The migration process in a polymer slab can be described by the second diffusion equation of Fick for uni-directional transport:[15]

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{5.2}$$

where C is the additive concentration (kg m^{-3}), t is the contact time (s), x is the position in the slab (m) and D is the diffusion coefficient (m^2 s^{-1}). Equation (5.2) was solved numerically for C(x,t) using the following initial and boundary conditions. [18]

Initial conditions: $C_{\mathrm{p}}(x,0) = \mathrm{C}_0$ (5.3)

$C_{\mathrm{s}}(0) = 0$ (5.4)

Boundary condition: $C_{\mathrm{p}}(0,t) = C_{\mathrm{P}}(L,t) = C_{\mathrm{s}}(t)$ (5.5)

where C_0 is the initial additive concentration in the polymer, L is the polymer thickness and x is the position which ranges from 0 to L.

The solution of equation (5.2) using equations (5.3)-(5.5) is based on the following assumptions:

1) Initially, the additive is homogeneously distributed throughout the polymer.
2) For the given polymer/additive/solvent-combination and temperature, the diffusion coefficient (D) is constant. Effects due to penetration of solvent into the polymer are ignored due to the low interaction between LDPE (δ = 16.96 M Pa^{½})

and ethanol (δ = 26.0 M Pa^{½}).[19] As the Irganox 1076 concentration in the polymer is low (<0.4%), concentration effects of Irganox 1076 itself are also ignored.

3) There is no concentration gradient in the solvent, as diffusion through the polymer is much slower than diffusion through ethanol. For comparison, the diffusion coefficient of Irganox 1076 in LDPE to ethanol at 40°C is 1×10^{-13} m^2 s^{-1},[17] whereas the diffusion coefficient of molecules in liquids under ambient conditions is in the order of magnitude of 10^{-9} m^2 s^{-1}.[20]
4) The partition coefficient of Irganox 1076 between polymer and ethanol is taken to have a value of 1. The results are not sensitive to this assumption. In the numerical simulation, the concentration in the polymer at the interface is assumed to be equal to the concentration in the solvent one time-step earlier. This assumption is justified as long as the step size in time is small. The concentration in the solvent was calculated using the mass balance equation (5.1).

5.3 Experimental

LDPE slabs, prepared by compression moulding, with a thickness of 1.6 mm, a density of 0.90 kg dm^{-3} and containing nominally 0.4% Irganox 1076 (octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl propionate), M=531 g mol^{-1}) were prepared and kindly provided by DSM (Geleen, The Netherlands).

Additive concentration profiles in the polymer were determined as follows. Polymer slab pieces of 2×2 cm^2 were separately incubated in closed jars containing 30 ml of ethanol in a water bath of 40°C. After different incubation times, the polymer pieces were removed from the ethanol, quickly surface dried using a smooth tissue and cooled to –20°C to stop the migration process. A piece of 1.2 cm^2 was punched out from the middle of each slab piece to avoid edge effects, after which the exact weight was measured on an analytical balance (Mettler Toledo). The microtome used was a Microm cryotome (Heidelberg, Germany) provided with cryolap knives (Adamas Instrumenten, Leersum, the Netherlands). Polymer slab pieces were mounted in the microtome using double-sided tesa-film (Beiersdorf, Germany). Slicing was performed parallel to the contact surface at –20°C. Slices of 20 µm each were collected three by three in pre-weighed vials and the exact weight of polymer per vial

(hereafter considered as one slice) was determined. The slices were extracted overnight with isooctane at 40°C, after which internal standard (hexadecyl-3,5-di-tert-butyl-4-hydroxybenzoate, Aldrich) was added. The extracts were analysed by GC-FID equipped with an on-column injector (GC 8000 series, Fisons Instruments) on a 15 m × 0.25 mm I.D. × 0.1 µm DB5-MS column (J&W Scientific) coupled to a 0.5 m × 0.25 mm I.D. × 30 nm retention gap (deactivated with OV-1701-OH, BGB Analytik). When the concentration was below the detection limit (0.1 $\mathrm{mgl^{-1}}$), the extracts were concentrated by evaporation under nitrogen.
The position along the thickness of the slab was calculated by:

$$x_j = \frac{1}{\rho A}\left(\sum_{i=1}^{j} M_i - \frac{1}{2} M_j\right) \tag{5.6}$$

where j is the current slice number, i is a counter for all previous slices, M is the slice mass, A is the surface area and ρ is the polymer density. The positions were calculated from the slice weight because the microtome did not cut slices of equal thickness.

Determination of Irganox 1076 concentration in ethanol as a function of time was carried out as described earlier,[17] except that the polymer slab pieces were fully immersed in the ethanol, instead of only on one side. A pre-weighed polymer slab piece of the same LDPE as used for the concentration profile experiments (also 4 $\mathrm{cm^2}$) was incubated at 40°C in a closed migration cell containing 30 ml ethanol, from which samples were drawn by a syringe as a function of time.

5.4 Results and discussion

The mass balance given by equation (5.1) for Irganox 1076 in polymer and solvent after different incubation times is presented in table 5.1. The total amount of Irganox 1076 in each polymer slab piece was obtained by summing up the amount in all slices of half the piece and, assuming a symmetrical profile, multiplying this value by two (as it was technically not possible to slice the whole polymer slab piece). Amounts of migrated Irganox 1076 in ethanol corresponding in time with the measurements in the polymer were obtained by interpolation of the curve of Irganox 1076 concentrations in

Table 5.1 Mass balance of Irganox 1076 in polymer and solvent standardized to a polymer mass of 1 g (symbols as explained in equation (1))

t (min)	M_P (mg) [1)]	M_S (mg) [2)]	$M_P + M_S$ (mg)	Deviation from $M_{initial}$ (%) [3)]
0	3.58 ($M_{initial}$)	0	3.58	0
235	3.37	0.40	3.77	5.2
975	3.23	0.59	3.82	6.7
1130	3.37	0.63	4.00	11.6
1455	3.08	0.70	3.78	5.6
14400	2.13	1.63	3.76	5.0
25920	1.56	2.13	3.69	3.1

[1)] sum of the amount in all slices of half the polymer slab piece multiplied by two

[2)] interpolated values of curve of Irganox 1076 concentration in ethanol as a function of time

[3)] Deviation calculated as: $\frac{(M_P + M_S) - M_{initial}}{M_{initial}} \cdot 100$

ethanol as a function of time. Ideally, the deviation, shown in the last column, should be zero.

The maximum deviation of 11.6% is therefore rather high. However, the average deviation is 6.2%, which is acceptable considering errors introduced by the analytical procedure. The deviation in all cases was slightly positive; one cause is that migration not only occurred from the two surface sides, but also from the edges, giving a higher amount of Irganox 1076 in ethanol than expected.

Figure 5.1(a)-(g) shows the experimental data at seven incubation times at 40°C together with the best fitting physical model given by equation (5.2) using the least square error criterion[18] for all observations simultaneously.

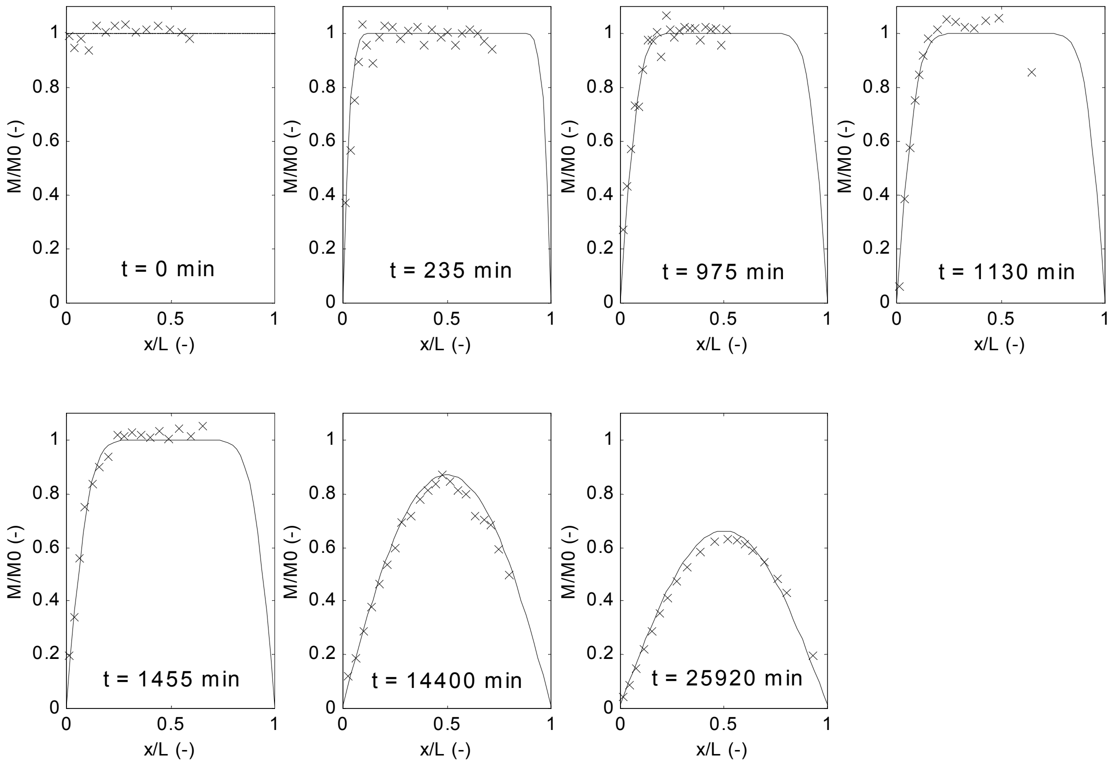

Figure 5.1 Concentration profiles of Irganox 1076 in LDPE for seven different contacting times expressed as the amount in the polymer at time *t* relative to the initial amount in the polymer per unit polymer weight. Experimental data is shown by crosses and the best fitting curve by solid lines.

Figure 5.1(a) confirms that the additive was initially homogeneously distributed in the polymer. If one considers each point as a separate estimate of the initial concentration, the average initial concentration was 3.58 mg g^{-1} (S.D. = 0.11 mg g^{-1}, n = 14). The model fits the experimental data quite well throughout the whole process. The diffusion coefficient obtained was 1.1×10^{-13} m^2 s^{-1}. Table 5.2 shows the diffusion coefficients obtained from individual fits of the concentration profile of each incubation time. The average of these diffusion coefficients is again 1.1×10^{-13} m^2 s^{-1}. It should be noted that only those points inside the polymer from which Irganox 1076 has actually migrated contribute to the estimation of the diffusion coefficient. For short times, Irganox 1076 has only migrated from *x*-positions near the contacting surface, resulting in few points actively contributing to the estimation of the diffusion coefficient. So when concentration profiles cannot be determined during the whole

Table 5.2 Diffusion coefficients from individual fits of the concentration profile in the polymer at each time

t (min)	D ($m^2 s^{-1}$) $\times 10^{14}$
235	14
975	8.4
1130	9.8
1455	9.0
14400	12
25920	12

migration process, the diffusion coefficient is best estimated using longer contacting times.

Assumption (3) (that there is no concentration gradient in the solvent) was checked by measuring two concentration profiles under gentle shaking of the solvent. Figure 5.2 shows the concentration profiles inside the polymer and the best fitting curve after 235 min and 1130 min in ethanol under gentle shaking (80 rotations/min) in a water bath of 40°C. The diffusion coefficient obtained was 1.3×10^{-13} m^2 s^{-1}, which is not significantly different from the diffusion coefficient obtained for the process with stationary ethanol (D=1.1×10^{-13} m^2 s^{-1}). Thus, the solubility and diffusion of Irganox 1076 in ethanol seems indeed high enough to justify the assumption of no concentration gradient in the solvent.

The diffusion coefficient obtained from the concentration profile measurements was compared with diffusion coefficients obtained from conventional measurements of concentration in the solvent in contact with the polymer as a function of time. The concentration of Irganox 1076 in the solvent (ethanol) as a function of time is shown in figure 5.3 together with the best fitting curve given by equation (5.2) according to the least square error criterion. For short incubation times, the model predictions are somewhat lower than the observed concentrations. This is caused by the fact that migration from the edges of the polymer slab piece was not negligible, as is assumed by the model.

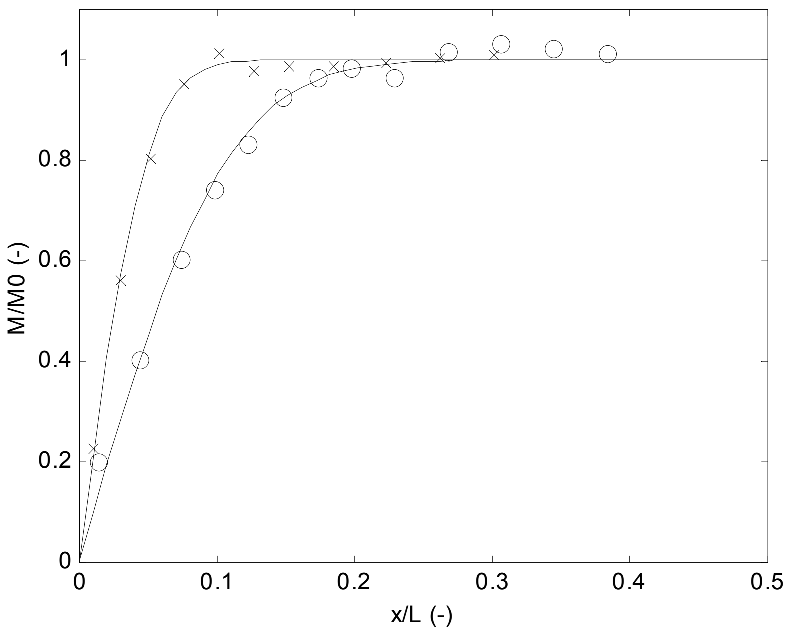

Figure 5.2 Concentration profiles of Irganox 1076 in LDPE in contact with ethanol after an contacting time of *t* = 235 min ('×') and t = 1130 min ('o') under gentle shaking, expressed as the amount in the polymer at time *t* relative to the initial amount in the polymer per unit polymer weight. The best fitting curve is shown by solid lines.

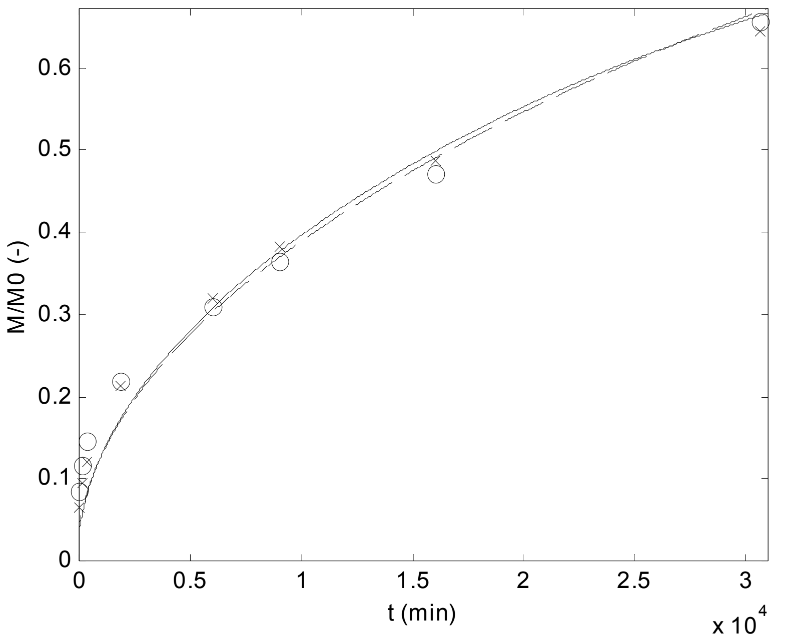

Figure 5.3 Migration of Irganox 1076 from LDPE into ethanol as a function of time expressed as the amount in the solvent at time *t* relative to the initial amount in the polymer per unit polymer weight. Experimental data of the duplicate measurements are shown by '×' and 'o' and the best fitting curves as solid and dotted lines, respectively.

This, as mentioned earlier, also explains some of the positive deviation found in the mass balance calculations. The diffusion coefficients obtained of the duplicate determinations were 1.1×10^{-13} m^2 s^{-1} and 1.6×10^{-13} m^2 s^{-1}. These values are comparable to the value obtained from the concentration profiles inside the polymer ($D = 1.1\times10^{-13}$ m^2 s^{-1}).

Finally, the method was applied to check the Arrhenius-type of equation[21] often found in rubbery polymers between the diffusion coefficient and the temperature given by

$$D = D_0 \exp(-\frac{E_D}{RT}) \tag{5.7}$$

where E_D represents the activation energy of diffusion (J mol^{-1}), R the gas constant (J mol^{-1} K^{-1}), T the temperature (K) and D_0 a pre-exponential factor (m^2 s^{-1}). Figure 5.4 shows that ln(D) as a function of the inverse temperature gives a straight line with a correlation coefficient of 0.98. The activation energy of diffusion is 113 kJ mol^{-1}, which is close to the value of 108 kJ mol^{-1} reported earlier for the diffusion of Irganox 1076 in LDPE measured in the same temperature range.[14]

5.5 Conclusions

A method using microtoming and GC-analysis for the determination of additive migration in polymers as a function of position and time has been validated for the combination LDPE/Irganox 1076/ethanol. The consistency of the mass balance was good and the concentration profiles inside the polymer could be described with the Fick diffusion equations. The diffusion coefficient obtained corresponded with that obtained from measurements of the Irganox 1076 concentration in ethanol as a function of time. The method is suitable for studying additive migration inside polymers as a function of both space and time. It is currently being applied to more complex migration processes including contacting solvents which cause swelling of the polymer. These will be presented in a future paper.

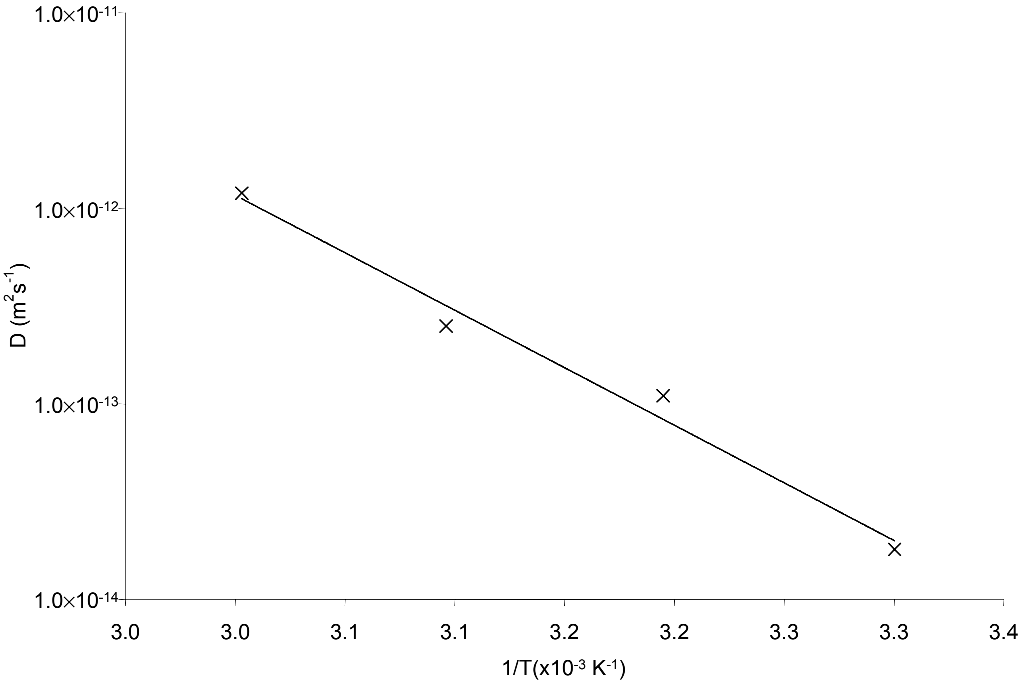

Figure 5.4 Diffusion coefficient of Irganox 1076 in LDPE in contact with ethanol as a function of temperature. Calculations were performed on concentration profiles of 20 hrs at 30°C, 18 hrs at 50°C and 16 hrs at 60°C, at 40°C the concentration profiles from figure 5.1 were used.

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6

Additive diffusion from LDPE slabs into contacting solvents as a function of solvent absorption[1]

Abstract

This article describes the simultaneous diffusion of a migrant and a solvent in low density polyethylene (LDPE). The migrant (Irganox 1076) moves out of the slab, while the solvent (isooctane, *n*-heptane or cyclohexane) moves inwards. Solvent absorption was measured separately by following the increase of the mass of the slab in time. It can be described by the Fick diffusion equation with a diffusivity depending on the solvent concentration, and an interface concentration depending on time. The final absorptions were 12% for isooctane, 14% for *n*-heptane and 29%for cyclohexane. Additive concentrations in the slab were determined at different positions by microtoming. Experiments were done for several contacting times. The concentration profiles were strongly affected by the solvent. A larger local solvent concentration increases the diffusivity of the migrant. The Fick equation with a migrant diffusivity depending on the solvent concentration gives a good description for the results with isooctane and *n*-heptane. The description is less good for the measurements with cyclohexane (when the polymer swells strongly).

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[1] submitted by I.E. Helmroth, M. Dekker and Th. Hankemeier

6.1 Introduction

There are many applications of polymers which require an understanding of diffusion of small molecules through the polymer. For example, in controlled release of pharmaceuticals, in active packaging and in packaging of food in polymers. An important problem affecting the diffusion rate occurs when the diffusion of the small molecules takes place simultaneously with absorption of solvent into the polymer. This process of simultaneous diffusion has not been studied adequately.

Diffusion of a non-volatile compound from a polymer into a contacting solvent depends on polymer properties such as physical state and degree of crystallinity, and on compound properties, such as size and shape. However, it also depends on solvent properties, in particular on the solubility of the solvent in the polymer and the solubility of the diffusing compound in the solvent. When the solvent hardly dissolves in the polymer diffusion of the compound from the polymer into the solvent can be described by the Fick diffusion equation with a constant diffusivity[1]. However, as the solubility increases a considerable amount of solvent is absorbed and deviations from this model arise. Due to swelling of the polymer, the diffusion rates of both the solvent and the compound will increase[1,2]. This type of diffusion is often described by an empirical equation, in which the diffusivity is an exponential function of solvent concentration[3-5] (see the theoretical part below). The equation has been shown to give a good description of the absorption and desorption of solvents in different polymers[6,7]. However, not much is known about the applicability of the equation to describe the diffusion of compounds with low molar present in the swelling polymer[8-10].

The purpose of this paper is to study how solvent absorption affects the diffusion of antioxidant Irganox 1076 in low density polyethylene (LDPE). We are interested to find out whether the simple equation for concentration dependent diffusivity can be used to describe additive diffusion using knowledge on solvent sorption parameters and the additive diffusion coefficient in the non-swollen polymer. Three solvents with different solubility in LDPE were selected: isooctane (2,2,4-trimethylpentane), *n*-heptane and cyclohexane. In all three solvents the antioxidant has a good solubility and they are all liquid at the experimental temperature of 40°C. Additive diffusion was determined by measuring concentration profiles in the polymer after different contact times. This is different from the commonly applied method of measuring additive concentrations in the solvent, since additive concentration is obtained as a function of both space and time. The applied method was evaluated and described earlier for diffusion in a non-swelling polymer[11].

6.2 Theory

Free-volume concept

Different empirical equations have been suggested for calculating concentration dependent diffusion coefficients in polymers[3,6-10,12-13]. The most common form is

$$D = D_0 \exp(\gamma c) \tag{6.1}$$

where D_0 ($m^2\ s^{-1}$) is the diffusion rate at infinite diffusant dilution (at $c = 0$), γ (-) is an adjustable parameter and $c = C/C_{max}$ (-), in which C is the solvent concentration (kg m^{-3}) and C_{max} the solubility of the pure solvent in equilibrium with the polymer (kg m^{-3}).

Equation (1) is considered to originate from the work of Doolitle[14], who described the fluidity of simple hydrocabon liquids using an exponential dependency between fluidity and available volume. Cohen and Turnbull[15] gave this relation a theoretical basis using the free-volume concept. According to this concept, there is a continuous redistribution of the *free-volume holes* between the molecules in a liquid, i.e. the space that is not occupied by the liquid molecules. Molecular transport occurs if a sufficiently large hole is formed next to a molecule, allowing a displacement of that molecule, and the original hole of the diffusing molecule is filled by another molecule. The diffusion coefficient is thus related to the probability of a molecule finding a free-volume hole of a specific size[16]. The free-volume concept was extended to diffusion in polymers by Fujita[17] and Vrentas and Duda[18]. Their equations, as well as equation (6.1), were derived in analogy with the Doolitle-equation. In this study, equation (6.1) was used due to its practical applicability and few model parameters.

Solvent diffusion

Solvent absorption by the polymer was described by the diffusion equation of Fick for diffusion in one dimension given by

$$\frac{\partial c^{\mathrm{s}}}{\partial t}=\frac{\partial}{\partial x}\left(D^{\mathrm{s}}\left(c^{\mathrm{s}}\right)\frac{\partial c^{\mathrm{s}}}{\partial x}\right) \tag{6.2}$$

where c^{s} (-) is the solvent concentration, x (m) the position along the thickness of the polymer slab, t (s) the time and D^{s} (m^2 s^{-1}) the diffusion coefficient depending on solvent concentration. Equation (6.2) was discretized as

$$c^{\mathrm{s}}_{i+1,j}=c^{\mathrm{s}}_{i,j}+\frac{\Delta t}{\Delta x^2}\left[D^{\mathrm{s}}_{i,j-0.5}\left(c^{\mathrm{s}}_{i,j-1}-c^{\mathrm{s}}_{i,j}\right)-D^{\mathrm{s}}_{i,j+0.5}\left(c^{\mathrm{s}}_{i,j}-c^{\mathrm{s}}_{i,j+1}\right)\right] \tag{6.3}$$

with i steps in time and j steps through the thickness of the slab. Concentration dependent diffusion coefficients were calculated by equation (6.1) that was discretized as

$$D^{\mathrm{s}}_{i,j\pm0.5}=D^{\mathrm{s}}_{0}\exp\left(\gamma^{\mathrm{s}}\,\frac{c^{\mathrm{s}}_{i,j}+c^{\mathrm{s}}_{i,j\pm1}}{2}\right). \tag{6.4}$$

Since the diffusion processes from the two opposite surface sides of the slab were considered to be symmetrical, only half of the slab thickness (L) was considered for estimation of the solvent absorption parameters. The center of the slab (x = 0) was assumed to be an isolated point with

$$\left[\frac{\partial c^{\mathrm{s}}}{\partial x}\right]_{x=0}=0 \tag{6.5}$$

which was discretized as

$$c^{\mathrm{s}}_{i,-1}=c^{\mathrm{s}}_{i,1}. \tag{6.6}$$

At the interface between polymer and solvent ($x = L$), the solvent concentration was assumed to attain its maximum value immediately, or a time dependent surface concentration was introduced given by[6]

$$\left[\tau \frac{\partial c^{\mathrm{s}}}{\partial t}\right]_{x=L} = \left[c_{\infty}^{\mathrm{s}} - c_{t}^{\mathrm{s}}\right]_{x=L} \tag{6.7}$$

where τ (s) is a first-order constant, c_t^{s} the surface solvent concentration at time t and c_{∞}^{s} the maximum surface solvent concentration (equal to 1 for calculations with dimensionless concentrations). Equation (6.7) was discretized as

$$c_{i+1,J}^{\mathrm{s}} = c_{i,J}^{\mathrm{s}} + \frac{\Delta t}{\tau}\left(c_{\infty}^{\mathrm{s}} - c_{i-1,J}^{\mathrm{s}}\right) \tag{6.8}$$

with step number J at $x = L$. At $t = 0$, the solvent concentration in the polymer was taken to be zero.

Additive diffusion

Similar to solvent absorption, additive diffusion from the polymer was described by

$$\frac{\partial c^{\mathrm{a}}}{\partial t} = \frac{\partial}{\partial x}\left(D^{\mathrm{a}}\left(c^{\mathrm{s}}\right)\frac{\partial c^{\mathrm{a}}}{\partial x}\right) \tag{6.9}$$

with c^{a} (-) the additive concentration and D^{a} ($\mathrm{m}^2\ \mathrm{s}^{-1}$) the additive diffusion coefficient depending on solvent concentration. Equation (6.9) was discretized similarly to equation (6.3) and additive diffusion coefficients were calculated by

$$D_{i,j\pm 0.5}^{\mathrm{a}} = D_0^{\mathrm{a}} \exp\left(\gamma^{\mathrm{a}} \frac{c_{i,j}^{\mathrm{s}} + c_{i,j\pm 1}^{\mathrm{s}}}{2}\right) \tag{6.10}$$

with D_0^{a} (m^2 s^{-1}) the additive diffusion coefficient at zero solvent concentration. Since additive concentration profiles were measured throughout the polymer slab, the total slab thickness was considered for additive concentration calculations. Solvent concentrations required for the additive concentration calculations were also carried out in this case for the total slab thickness, using equation (6.7) as boundary condition at both surface sides.

At the interface between polymer and solvent, the additive was assumed not to be influenced by any contact resistance since it was well soluble in all solvents. Under this assumption, the additive concentrations at the interface remain constant and the ratio of concentration differences between boundary and bulk will be proportional to the square root of the diffusion coefficients in polymer and solvent according to[4]

$$\frac{c_0^{\mathrm{a}} - c^{\mathrm{a}^*}}{c_{\mathrm{sol}}^{\mathrm{a}^*}} = \sqrt{\frac{D_{\mathrm{sol}}^{\mathrm{a}}}{D^{\mathrm{a}}}} \qquad (6.11)$$

where c_0^{a} (-) is the initial additive concentration in the polymer, c^{a^*} (-) is the additive concentration at the polymer side of the interface, $c_{\mathrm{sol}}^{\mathrm{a}^*}$ (-) the additive concentration at the solvent side of the interface and $D_{\mathrm{sol}}^{\mathrm{a}}$ the diffusion rate of additive in the solvent. Since the solvent volume was much larger than the polymer volume, the additive bulk concentration in the solvent was approximately equal to zero during the entire experiment. Equation (6.11) is valid as long as the additive concentration in the center remains constant, i.e. the slab can be considered as a semi-infinite medium. When the additive concentration in the center decreases, the assumption is no longer valid and the boundary concentrations will decrease.

Model parameters were estimated by minimizing the sum of squared errors between experimental and predicted values[19].

6.3 Experimental

Materials

Compression moulded slabs of LDPE with a density of 0.922 kg dm^{-3} and a nominal thickness of 1.61 mm were kindly provided by DSM Research (Geleen, the Netherlands). Slabs with and without Irganox 1076 (octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl propionate), at a concentration of 3300 mg kg^{-1}, were specially produced for this study.

Solvent absorption

Solvent absorption was measured by the mass uptake method[3]. Polymer slabs of 6 cm × 8 cm without additives were submerged in an excess of the solvent at 40°C. At predefined time intervals, the slabs were removed from the solvent, quickly surface dried and weighed on an analytical balance (Mettler Toledo, d = 0.001g), after which they were immediately placed back into the solvent. Measurements continued until no further mass increase could be detected. The mass change was assumed to be caused by solvent absorption only, since the maximum loss of low-molecular polymer parts into isooctane, *n*-heptane or cyclohexane was determined to be less than 0.7%.

Additive concentration profiles

Additive concentration profiles inside the polymer were determined by using the slicing method described in a previous paper[11]. Polymer slab pieces of 2 cm × 2 cm were immersed in the test solvent at 40°C during a predefined time period, after which the pieces were cooled to –20°C to stop the diffusion process. A circle with an area of 1.33 cm^2 was punched from the center of the polymer slab and sliced perpendicularly to the main surface sides. Slices of approximately 20 μm thickness were collected three by three in pre-weighed vials, the absorbed solvent was allowed to evaporate for at least one hour, after which the vials were weighed and the slices were extracted with isooctane. Additive concentration was determined by analysing the extracts with gas chromatography with a flame ionization detector (GC-FID) (for details see ref. [11]). Concentrations were calculated per mass of polymer and normalized to the initial additive concentration in the polymer. For the diffusion process the actual concentration in the swollen polymer matrix determines the transport rate. By using the concentration per mass of polymer the additive concentration is therefore overestimated to some extent. However, a correction of this overestimation using information on solvent absorption would introduce even more uncertainty, since the local amount of solvent in each slice would have to be obtained from simulations based on the experimental mass-time curve. The overestimation in additive concentration is therefore neglected in this paper.

The position along the thickness of the slab was calculated by relating the mass of the slices in each vial (after evaporation of the absorbed solvent) to the total mass of all slices. These values were converted to positions by using the measured final thickness of the polymer slab piece. Because of local variation in the uptake of solvent (more on the edge and less in the center) this conversion leads to an underestimation of the step size at the edge and an overestimation of the step size in the center of the polymer slab. Since the thickness increase of the polymer for the solvents and exposure times used is estimated to be lower than 10% this will result in a maximum of 10% larger actual step size than is used for converting the experimental data. This means that the actual concentration gradient is less than 10% smaller than the calculated one and this difference is here considered to be negligible. The influence of this and before mentioned assumption on the results will be discussed in the next section.

6.4 Results and discussion

Mass uptake curves of isooctane, *n*-heptane and cyclohexane by the LDPE slabs at 40°C are shown in figure 6.1. Equilibrium was reached within 10 hours with *n*-heptane, 15 hours with cyclohexane and 25 hours with isooctane. The maximum mass uptake of the three solvents was 29% (w/w) for cyclohexane, 14% (w/w) for *n*-heptane and 12% (w/w) for isooctane. The solubility of molecules in polymers generally decreases with increasing molar mass[20]. The molar mass of cyclohexane, *n*-heptane and isooctane are 84 g mol^{-1}, 100 g mol^{-1} and 114 g mol^{-1}, which confirms this general trend.

Remarkably, cyclohexane is absorbed twice as much as *n*-heptane. This shows that solubility is also affected by molecular shape. This may be explained as follows. For the linear heptane molecules, it is entropically more favourable to be in solution than between the polymer chains since in the latter case their freedom of rotation is restricted. For the cyclic cyclohexane molecules, the difference in number of degrees of freedom between being in

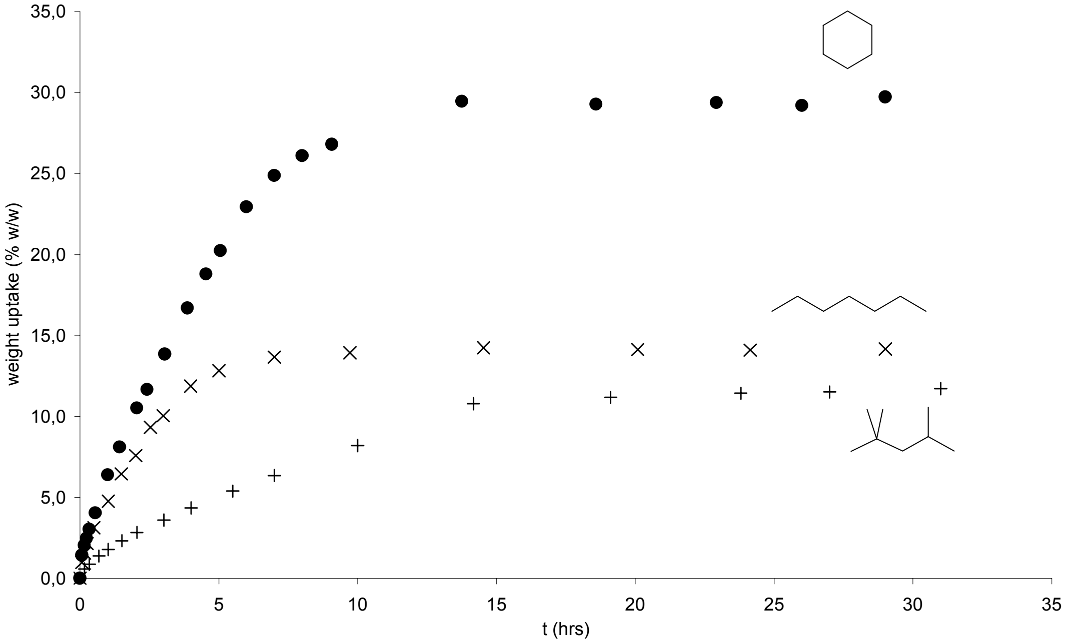

Figure 6.1 Mass uptake curves of cyclohexane (•), n-heptane (×) and isooctane (+) by LDPE slabs with thickness 1.6 mm at 40°C. Points are average data of at least two measurements. The molecular structure of each solvent is illustrated next to the corresponding curve.

solution or within the polymer is less. So diffusion into the polymer will therefore be entropically more favourable for cyclohexane than for *n*-heptane.

The s-shaped curve of the mass uptake as a function of the square root of time (fig. 6.2) shows that the sorption of these solvents cannot be described as Fickian diffusion with constant diffusivity, which would have given a straight initial line. In rubbery polymers, it is generally assumed that chain relaxation of the polymer molecules is rapid compared to sorption, which implies that diffusivity is only a function of concentration as described by equation (6.1)[3]. Figure 6.3 shows the fit of equations (6.1) to (6.6) to the sorption data of heptane with D_0^s = 6×10^{-13} m^2s^{-1} and γ^s = 4.8. The model gives a reasonable, though not perfect, description of the experimental data. This result is in accordance with that for the sorption of hexane in LDPE and natural rubber obtained by Hedenqvist[6], who showed that a model using a

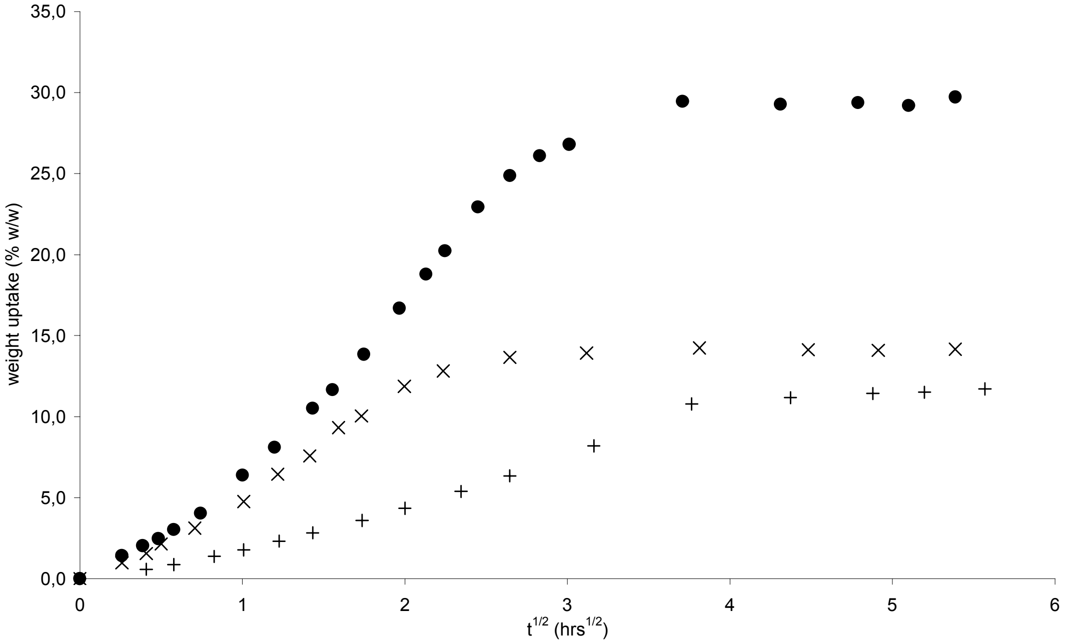

Figure 6.2 Mass uptake curves as a function of the square root of time of cyclohexane (•), n-heptane (×) and isooctane (+) by LDPE slabs with thickness 1.6 mm at 40°C. Points are average data of at least two measurements.

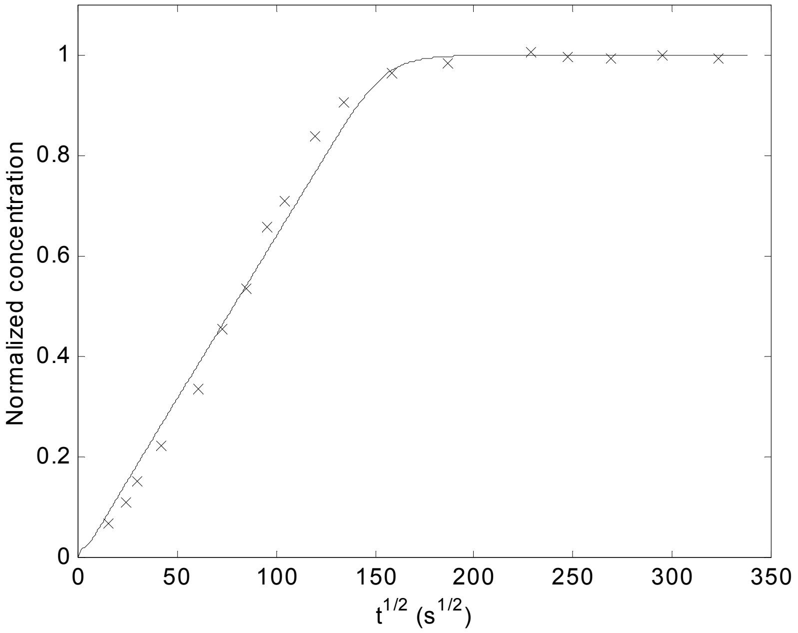

Figure 6.3 Fit of equations (6.1)-(6.6) to the sorption data of heptane in LDPE with D_0^s = 6×10^{-13} m^{2}s^{-1} and $\gamma^s = 4.8$. Experimental data shown by '×' and predicted data by a solid line.

concentration dependent diffusivity only, does not lead to an s-shaped curve and that the concentration in the polymer at the interface must depend on time. Hedenqvist and colleagues therefore suggested to include the boundary condition in eq. (6.7). The reason for this time dependency is considered to be that the swollen surface is subjected to compressive stresses caused by the non-swollen parts within the polymer[3,6]. At the polymer surface, the maximum solvent concentration is not instantly reached, but only after a certain time-lag. Two model parameters are introduced, namely an initial surface concentration c_0^s and a first-order constant τ. Figures 6.4, 6.5 and 6.6 show that indeed good fits to the three experimental sorption curves were obtained by including a time dependent surface concentration. Estimated model parameters are given in table 6.1. This result does not prove that a time dependent surface process takes place, but the improvement of the fits motivated us to use this model for further calculations.

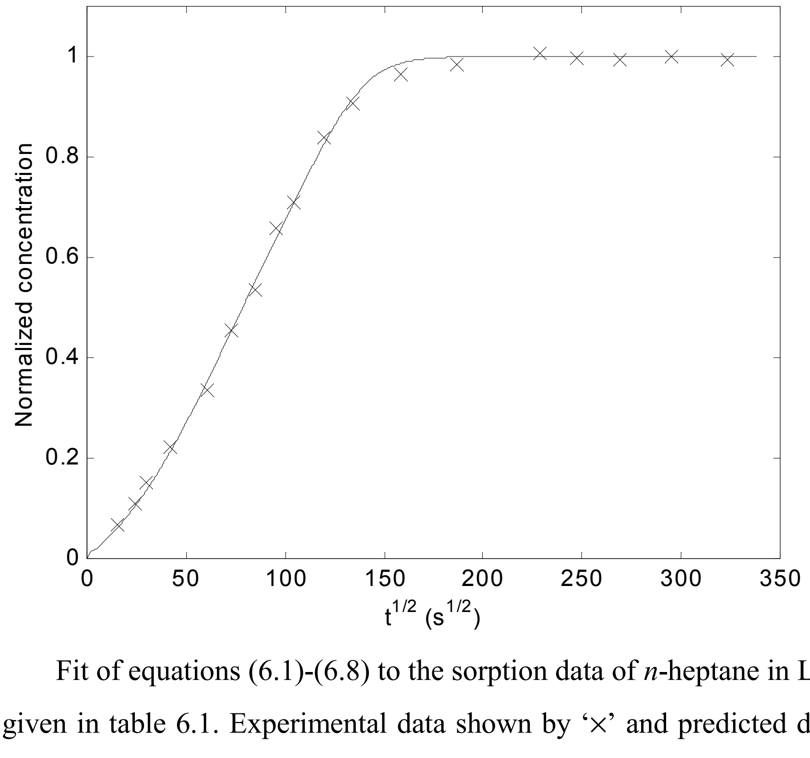

Figure 6.4 Fit of equations (6.1)-(6.8) to the sorption data of *n*-heptane in LDPE with the parameters given in table 6.1. Experimental data shown by '×' and predicted data by a solid line.

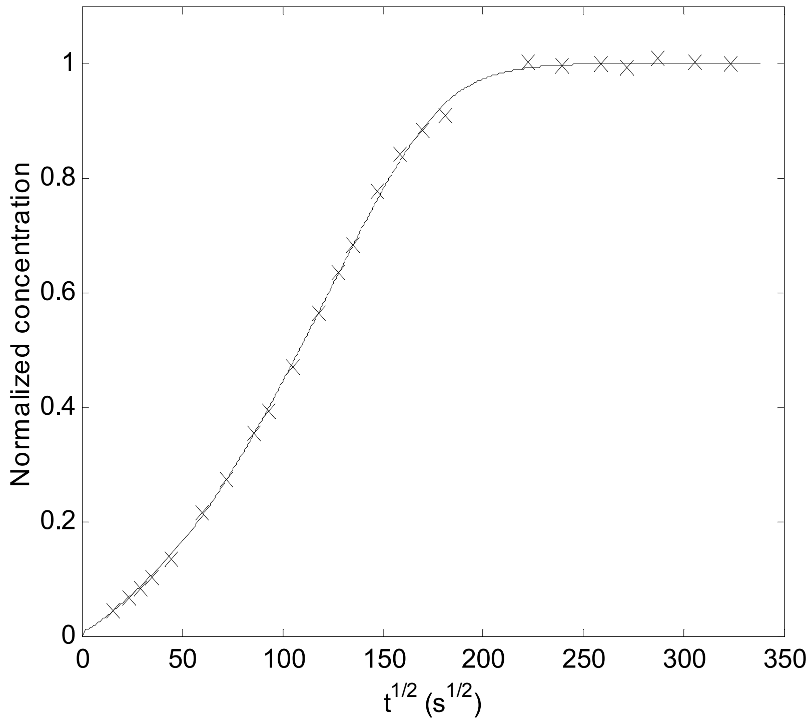

Figure 6.5 Fit of equations (6.1)-(6.8) to the sorption data of cyclohexane in LDPE with the parameters given in table 6.1. Experimental data shown by '×' and predicted data by a solid line.

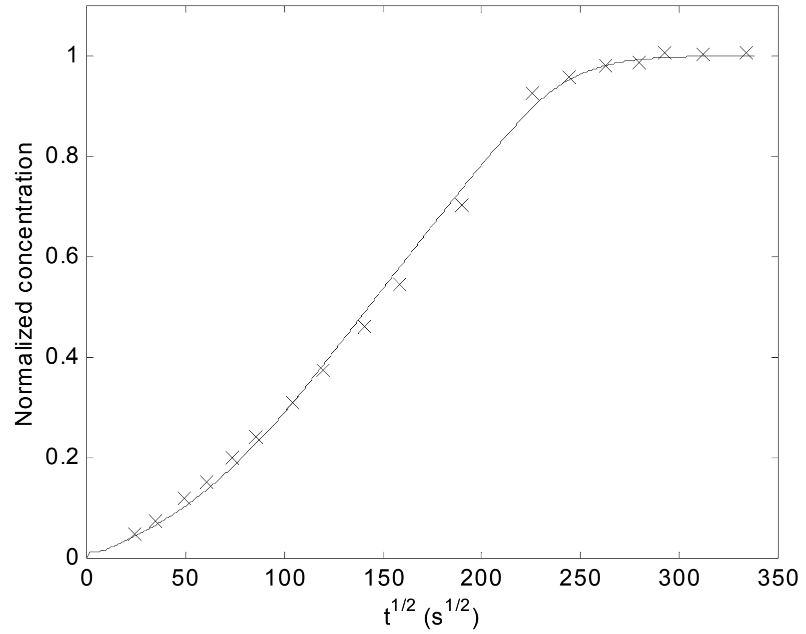

Figure 6.6 Fit of equations (6.1)-(6.8) to the sorption data of isooctane in LDPE with the parameters given in table 6.1. Experimental data shown by '×' and predicted data by a solid line.

Table 6.1 Estimated parameters for the absorption of the test solvents into LDPE slabs at 40°C.

	isooctane	*n*-heptane	cyclohexane
D_0^{s} (m^2 s^{-1})	5.2×10^{-13}	2.4×10^{-12}	3.4×10^{-12}
γ^{s} (-)	4.0	3.4	2.4
τ (h)	1.9	0.56	1.8
c_0^{s} (-)	0.67	0.75	0.64

The concentration profiles of Irganox 1076 diffusing from the LDPE slabs into the three test solvents are shown in figures 6.7, 6.8 and 6.9. Also shown in these figures are the fits of equations (6.9) to (6.11) to the experimental concentration profiles, taking into account the solvent concentrations simulated by equations (6.1) to (6.4), (6.7) and (6.8) with the parameters given in table 6.1. D_0^{a} in equation (6.10) is the value of the diffusion coefficient for zero solvent concentration (the non-swollen polymer). This value of 1.1×10^{-13} m^2 s^{-1} was obtained from the diffusion of Irganox 1076 from the LDPE slab into ethanol[10]; ethanol is hardly absorbed by LDPE.

The additive concentration at the interface between polymer and solvent, according to equation (6.11), was determined by extrapolation from the experimental additive concentrations. Estimated values of γ^{a} are given in table 6.2.

Table 6.2 Estimated parameters for the diffusion of Irganox 1076 from LDPE slabs into the test solvents at 40°C.

	γ^{a} (-)
isooctane	4.2
n-heptane	4.9
cyclohexane	6.9

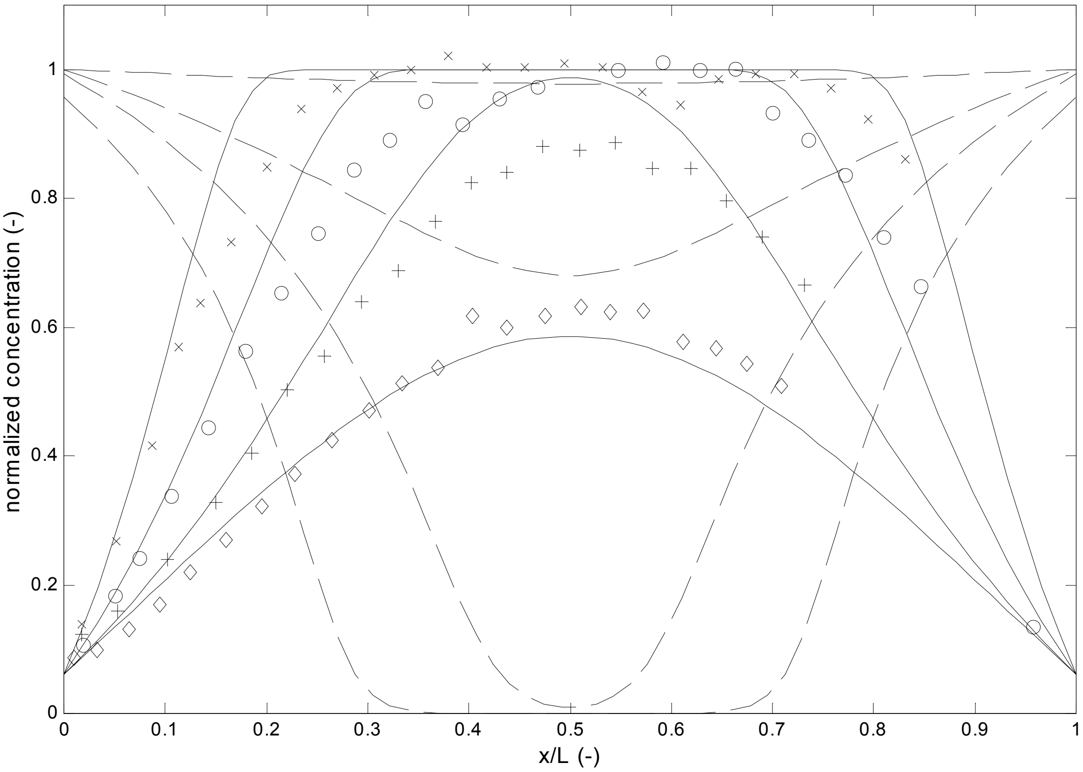

Figure 6.7 Fit of equations (6.1)-(6.4), (6.7)-(6.13) to the experimental concentration profiles of Irganox 1076 diffusing from the LDPE slab into *n*-heptane after 1 ('×'), 2 ('o'), 4 ('+') and 7 ('◊') hours using the parameters given in table 6.1 and 6.2. Predicted additive concentrations are shown by a solid line and predicted solvent concentrations by a dashed line (notice that the solvent is being absorbed by the slab while the additive is diffusing out from the slab).

The experimental data clearly show that additive diffusion is affected by solvent absorption. The decrease of the additive concentrations within the LDPE slab as a function of time is the quickest for cyclohexane and slowest for isooctane. This result was expected since cyclohexane has the highest solubility in LDPE and thus adds most free-volume to the polymer, resulting in a higher diffusion rate of the additive.

The model curves give a reasonable prediction of the additive diffusion as a function of time. However, systematic deviations between experimental and predicted concentrations are observed. The predicted concentration gradient is generally steeper

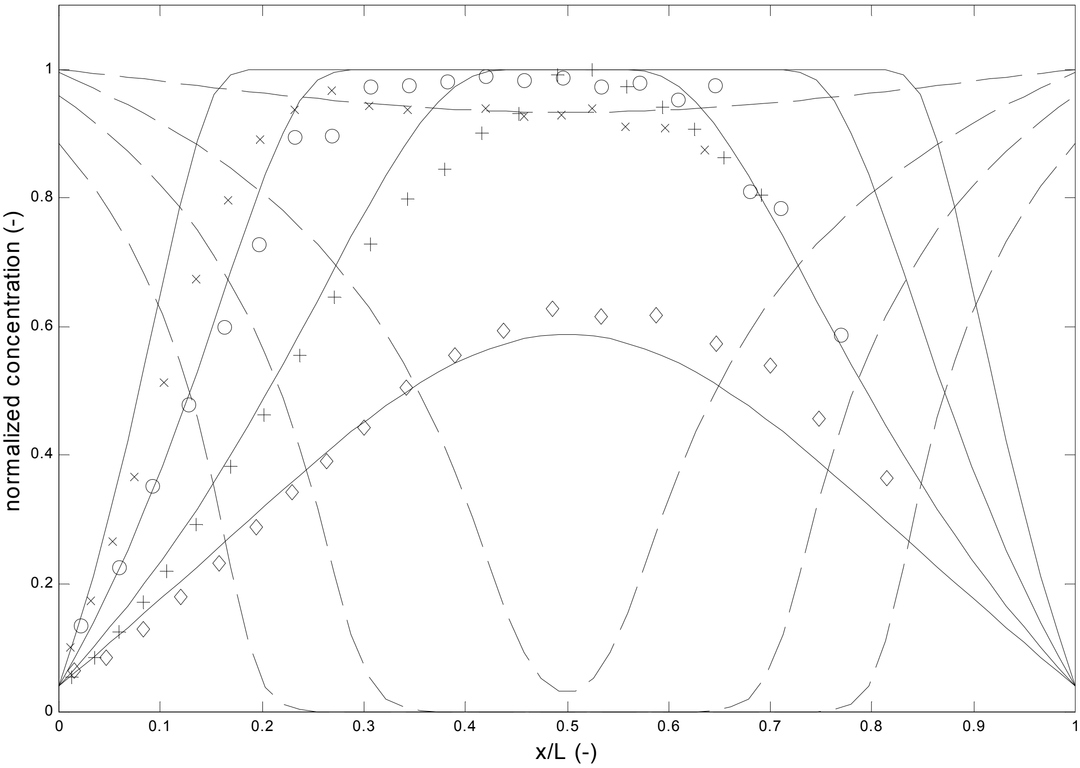

Figure 6.8 Fit of equations (6.1)-(6.4), (6.7)-(6.13) to the experimental concentration profiles of Irganox 1076 diffusing from LDPE slabs into isooctane after 2 ('×'), 4 ('o'), 8 ('+') and 17 ('◊') hours with the parameters given in table 6.1 and 6.2. Predicted additive concentrations are shown by a solid line and predicted solvent concentrations by a dashed line (notice that the solvent is being absorbed by the slab while the additive is diffusing out from the slab).

than the experimental one. Consequently, predicted concentrations are slightly lower than experimental values near the edge and higher near the center, particularly for cyclohexane. The deviations could be due to either the model description or the experimental set-up. Some considerations concerning the calculation of the *x*-positions of and the additive concentration in each slice due to solvent absorption were discussed in the experimental part. As shown in table 6.3, the assumption of a maximum increase of thickness of 10% at the different contacting times is indeed acceptable. Some of the deviation may be due the use of concentrations based on polymer mass (converted to volume) instead of the total mass of polymer and solvent.

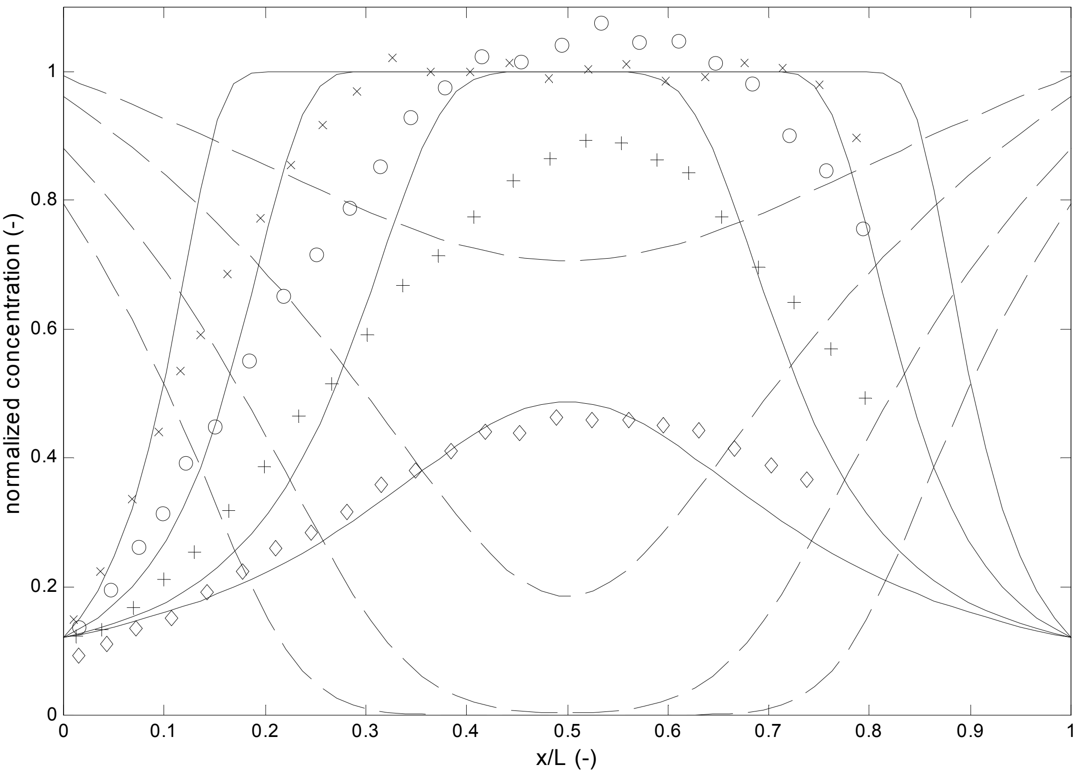

Figure 6.9 Fit of equations (6.1)-(6.4), (6.7)-(6.13) to the experimental concentration profiles of Irganox 1076 diffusing from LDPE slabs into cyclohexane after 1 ('×'), 2 ('o'), 4 ('+') and 7 ('◊') hours with the parameters given in table 6.1 and 6.2. Predicted additive concentrations are shown by a solid line and predicted solvent concentrations by a dashed line (notice that the solvent is being absorbed by the slab while the additive is diffusing out from the slab).

Table 6.3 Thickness increase of polymer slab in the test solvents after different contact times.

Cyclohexane		*n*-heptane		isooctane	
t (h)	%	t (h)	%	t (h)	%
1	7.1	1	4.1	2	2.8
2	8.5	2	4.9	4	3.5
4	9.8	4	6.7	8	4.5
7	12.0	7	6.8	17	5.5

In contrast with the results for ethanol[11], the additive concentrations at the interface between polymer and solvent were not zero for the solvents used in this study. This may be explained by looking at equation (6.11), which shows that the ratio of concentration differences between boundary and bulk are proportional to the square root of the relative diffusion rates in the polymer and solvent. When solvent is absorbed by the polymer, the additive diffusion coefficient in the polymer increases and the difference between the initial additive concentration and the concentration at the boundary on the polymer side at time *t* will decrease. The higher the absorption, the closer the diffusivity will be to that in the solvent (approximately 10^{-9} m^2 s^{-1}) and the higher the boundary concentration will be. This theory is confirmed by the result that the boundary concentration was the highest for cyclohexane and the lowest for isooctane.

Even when experimental uncertainties are taken into account, it seems that equation (6.1) is not fully adequate to describe the additive diffusion as a function of time. Especially for high solvent absorption, the constraint of using the diffusion coefficient in the non-swollen polymer has to be compensated for by an extremely steep concentration gradient. This results in a large value of γ^a for diffusion into cyclohexane. It should be noted that this result can only be observed by measuring additive concentration profiles in the polymer. Measurements in the contacting solvent as a function of time give only the integrated amount of additive that has diffused into the solvent and provide no information on the distribution.

6.5 Conclusions

The empirical equation relating diffusion coefficients of compounds in a polymer to concentration according to the free-volume theory has been used to describe the complex process of additive diffusion from an LDPE slab into a contacting solvent taking place simultaneously with solvent absorption. For a solvent absorption of less than 15% (w/w), concentration profiles were fairly well predicted. For a higher solvent absorption, of 29% (w/w), the equation was not able to describe the diffusion process adequately.

The importance of measuring concentrations of the diffusants in the polymer as a function of both time and place is emphasized by the results obtained in this study. The measurement method used here, microtoming of the polymer slab, is straightforward and gives good results. However, it still needs to be improved at some points that have been discussed. Sophisticated imaging techniques, like microscopy FTIR or Raman, may be good alternatives to microtoming, especially for measuring both solvent and additive concentrations inside the polymer. The challenge will be to convert obtained signals to real concentrations.

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7

Questions and Recommendations

7.1 Are predictive migration models useful?

Predictive migration modelling can be a useful tool both for material development and for certification of existing or new materials. A macroscopic Fick model with two parameters (diffusion coefficient *D* and partition coefficient *K*) seems appropriate for most food-packaging situations. A key question is how to obtain model parameter values. Deriving diffusion and partition coefficients from intrinsic material parameters (such as free-volume space or compound solubility) remains difficult due to a lack of sufficient knowledge about the physics of these relationships. Two different methods of obtaining diffusion coefficient values have been treated in this thesis: (1) direct experiments with the given material, and (2) prediction on the basis of results in literature using a stochastic approach. The choice of method will depend on two questions:

(1) What is the required precision of the prediction?

(2) Does the given material have diffusion properties similar to materials tested in literature?

The answer to the first question depends on the purpose of the prediction. For regulatory purposes, the predicted value must be on the safe side. Unless the predicted value is near the critical value, the exact value is not important. For those cases that the diffusion process is indeed important, it has been shown that exact values of the diffusion coefficient can be measured and for example used in calculations on packaging dimensions.

The second question is only relevant for materials on which a large number of diffusion data is available in literature. If so, then it is possible to apply a stochastic approach. Extrapolation to materials that are hardly known in literature will greatly decrease the precision of the predicted value.

7.2 Can we predict the effect of solvent absorption on additive migration?

For the purpose of this thesis, we must first consider whether there is an effect of solvent absorption on additive migration in real food/packaging situations. For LDPE, no effect was found for the migration of Irganox 1076 into olive oil. Also no effect was found for the triglycerides tributyrin and tricaprylin. These results indicate that the migration rate of migrants with a molar mass similar to or smaller than Irganox 1076 is not increased when the plastic is in contact with given fatty food simulants. It would be interesting to see the results for different polymer types and compounds with higher molar mass.

For those situations where solvent absorption does occur, it should be included in a predictive model. The semi-empirical free volume equation can describe additive migration reasonably well for a solvent absorption less than 15%. For this type of prediction, knowledge of the diffusion coefficient in non-swollen polymer is required as well as the value of one model parameter γ which must be determined from absorption measurements. (See for instance the results of Reynier (2001) for compound diffusion in LDPE, HDPE and PP.)

7.3 How to proceed?

The work in this thesis shows that coupled diffusion processes in polymers are not yet fully understood. Further research is therefore necessary. On one hand by practical experiments, preferably by measurements of concentrations within the polymer using microtoming and/or imaging techniques. During this research project, two imaging techniques were tested for migration measurements. One was Confocal Laser Scanning Microscopy (CLSM) (de Grauw 1998) and the other Laser Ablation Inductively Coupled Plasma Mass Spectroscopy (LA-ICP-MS) (Mank 2000). Both techniques showed some interesting results, but turned out to give problems due to the molecules used and the low concentration. Since too much time would have been

required to obtain successful results, the methods could not be further developed. It is however highly recommended to continue the research with these, and other, techniques.
On the other hand molecular simulations (Hedenqvist *et al*. 2002) may be well suited to obtain more theoretical insight into diffusion on a microscopic scale. At present, these methods are only applicable to very simple structures of polymer and additive. More research is thus still also needed in this area.

Important is also the continuation of applied migration research, especially since predictive migration models have been approved of in EC packaging legislation. A first evaluation of the current ‘Piringer’ model has been carried out in this thesis and a different (stochastic) approach has been suggested. In order to improve this approach, the measurement of new migration data for different compounds and polymers is highly recommended.

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Summary

Food is very often in contact with plastics in packaging, devices or bulk storage vessels. An important problem is the migration of compounds with small molar mass (such as plasticizers, antioxidants and UV stabilizers) from the plastic into the food. In Europe migration is regulated by EC Directives and, in case these are absent, by national legislation. Migration experiments are carried out to demonstrate that a material in contact with food complies with these regulations. These experiments are time-consuming and expensive, so there is an increasing interest in predicting migration using mathematical diffusion models.

The objectives of this thesis are (1) to investigate the possible use of predictive migration modelling for legislative purposes and to evaluate different modelling approaches and, (2) to study the effect of solvent absorption by the plastic on migration.

In Chapter 2 a brief theory is given on migration. Of main importance are the size and shape of the migrants, the density, crystallinity and degree of crosslinking and branching of the polymer, the solubility of migrant in solvent and solubility of solvent in polymer and the temperature. A deterministic, a worst-case and a stochastic approach to predict diffusion coefficients were compared. All approaches give a reasonable, but rough, estimation of the diffusion coefficient. In contrary to deterministic models, stochastic models take natural and experimental variations into account by predicting the most probable outcome based on a large number of data from earlier experiments. The background of the stochastic approach to predict diffusion coefficients is presented in chapter 3. Probability distributions were derived from plots of diffusion coefficients as a function of the molar mass of migrants in the polymers LDPE and LLDPE, MDPE and HDPE, and PP at a temperature of 23°C. A large number of published experimental diffusion coefficients was used. The experimental data can be described by a log-normal distribution. The method presented provides information on the probability distribution for migration from a given packaging/food simulant combination. This is important for prediction of the probability that a given migration limit may be exceeded.

Chapters 4 to 6 are on the simultaneous diffusion of a migrant (Irganox 1076) and a solvent in the polymer LDPE. The migrant diffuses out of the polymer, while the solvent is diffusing inwards.

In chapter 4, the influence of different contacting solvents was tested: ethanol, isopropanol, isooctane, ethylacetate, cyclohexane, tributyrin, tricaprylin and olive oil. The concentration of Irganox 1076 in the liquid contacting the polymer was measured as a function of time. From this curve a diffusion coefficient and a partition coefficient were obtained using the Fick diffusion equation. The equilibrium uptake of solvent by the polymer was measured separately. For solvents with low molar mass the diffusion coefficient of Irganox 1076 increases with increasing solvent uptake. For the two tri-glycerides and olive oil no increase of the diffusion coefficient was found upon solvent absorption (only 1-2%) by the polymer.

The aim of chapter 5 was to test a method for the measurement of additive concentration profiles inside the polymer slab. The contacting solvent was ethanol. The local concentrations of Irganox 1076 were determined for different times as a function of position. This was done by microtoming and GC-analysis. The measured concentration profiles were well described by the Fick diffusion equation. The diffusion coefficient obtained agreed with the value obtained from following the Irganox 1076 concentration in the solvent as a function of time.

In chapter 6 the diffusion of Irganox 1076 and solvent were both measured as a function of time. Solvents tested were isooctane, *n*-heptane and cyclohexane. Solvent absorption was measured by following the increase of the mass of the slab as a function of time. It could be described by the Fick diffusion equation with a diffusivity depending on the solvent concentration, and an interface concentration depending on time. Additive concentrations were determined at different positions in the slab for several contacting times by the method tested in chapter 5. The shape and the dynamics of the concentration profiles were strongly affected by the solvent. The Fick equation with a migrant diffusivity depending on the solvent concentration gave a good description for the results with isooctane and *n*-heptane. The description is less good for the measurements with cyclohexane (when the polymer swells strongly).

Samenvatting

Levensmiddelen komen vaak in contact met plastics in verpakkingen, apparaten of opslagcontainers. Een belangrijk probleem hierbij is dat stoffen met een lage molaire massa (bijvoorbeeld weekmakers, antioxidanten en UV stabilisatoren) vanuit het plastic in het levensmiddel kunnen migreren. In Europa is migratie wettelijk geregeld in EC Directieven en, in geval deze er niet zijn, door nationale wetgeving. Migratie-experimenten worden uitgevoerd om aan te tonen dat een materiaal dat in contact komt met levensmiddelen voldoet aan de wetgeving. Deze experimenten zijn tijdrovend en duur, dus er is een toenemende interesse in het voorspellen van migratie door middel van wiskundige diffusiemodellen.

De doelstellingen van dit proefschrift zijn (1) onderzoek naar het mogelijk gebruik van voorspellende migratiemodellen voor wetgevingsdoeleinden en evaluatie van verschillende modelaanpakken, en (2) bestuderen van het effect van solvent absorptie op migratie.

In hoofdstuk 2 wordt een korte theorie gegeven van migratie. Van groot belang zijn de grootte en vorm van de migranten, de dichtheid, kristalliniteit en mate van cross-linking en vertakking van het polymeer, de oplosbaarheid van migrant in de solvent en oplosbaarheid van solvent in polymeer en de temperatuur. Een deterministische, een worst-case en een stochastische aanpak voor het voorspellen van diffusie-coëfficiënten werden vergeleken. Alle aanpakken geven een redelijke, maar ruwe, schatting van de diffusie coëfficiënt. In tegenstelling tot deterministische modellen houden stochastische modellen rekening met natuurlijke en experimentele variaties door de meest waarschijnlijke uitkomst te berekenen op basis van resultaten van een groot aantal eerdere experimenten. De stochastische aanpak voor het schatten van diffusie coëfficiënten wordt beschreven in hoofdstuk 3. Waarschijnlijkheids-verdelingen werden afgeleid uit figuren van diffusie coëfficiënten als functie van het molaire gewicht van migranten in de polymeren LDPE en LLDPE, MDPE en HDPE, en PP bij een temperature van 23°C. Een groot aantal gepubliceerde experimentele diffusie coëfficiënten werd hiervoor gebruikt. De experimentele data kunnen worden beschreven door een log-normale verdeling. De beschreven methode geeft informatie over de waarschijnlijkheidsverdeling voor de migratie in een gegeven combinatie van verpakking en levesnmiddel. Dit is belangrijk voor het voorspellen van de waarschijnlijkheid dat een bepaalde migratielimiet zou worden overschreden.

De hoofdstukken 4 tot en met 6 gaan over de gelijktijdige diffusie van een migrant (Irganox 1076) en een solvent in het polymer LDPE. De migrant diffundeert uit het polymeer, terwijl het solvent het polymeer in diffundeert.

In hoofdstuk 4 werd de invloed van verschillende vloeistoffen getest: ethanol, isopropanol, isooctaan, ethylacetaat, cyclohexaan, tributyrin, tricaprylin and olijfolie.

De concentratie Irganox 1076 in de solvent in contact met het polymeer werd gemeten als functie van de tijd. Uit deze curve werden een diffusiecoëfficiënt en een verdelingscoëfficiënt geschat aan de hand van de diffusievergelijking van Fick. De hoeveelheid door het polymeer opgenomen solvent bij evenwicht werd afzonderlijk gemeten. Voor solvents met een lage molaire massa neemt de diffusie-coëfficiënt toe bij toenemende solventopname. Voor de triglyceriden en olijfolie werd geen toename van de diffusie-coëfficiënt gevonden bij opname (slechts 1-2%) door het polymeer.

Het doel van hoofdstuk 5 was het testen van een methode voor het meten van concentratieprofielen van additief binnen in het polymeer. De contactvloeistof was ethanol. De plaatselijke Irganox 1076 concentraties werden bepaald voor verschillende tijden als functie van de plaats. Dit werd gedaan door de polymeerplaat te microtomen en het extract te analyseren met behulp van GC. De gemeten concentratieprofielen werden goed beschreven door de diffusievergelijking van Fick. De diffusie-coëfficiënt kwam overeen met de waarde verkregen door het volgen van de Irganox 1076-concentratie in het solvent als functie van de tijd.

In hoofdstuk 6 werd de diffusie van zowel Irganox 1076 als solvent gemeten als functie van de tijd. Geteste solvents waren isooctaan, *n*-heptaan and cyclohexaan. Solventopname werd gemeten door de massatoename van de polymeerplaat te volgen als functie van de tijd. Deze kon worden beschreven door de diffusievergelijking van Fick met een diffusiesnelheid die afhangt van de solventconcentratie, en een tijdsafhankelijke randconcentratie. Additiefconcentratie werden gemeten op verschillende plaatsen in de polymeerplaat met de methode uit hoofdstuk 5. De vorm en het verloop van de concentratieprofielen werden sterk beïnvloed door het type solvent. Een grotere plaatselijke solventconcentratie zorgde voor een toename van de diffusiesnelheid van het migrant. De diffusievergelijking van Fick waarbij de diffusiesnelheid van het migrant afhangt van de solventconcentratie gaf een goede beschrijving van de resultaten voor isooctaan and *n*-heptaan. De modelbeschrijving is minder goed voor de metingen met cyclohexaan (waarbij sterke zwelling optreedt van het polymeer).

Dankwoord

Tot slot nog enkele woorden van dank aan een aantal mensen die mij geholpen hebben bij het tot stand komen van dit proefschrift.

Allereerst wil ik TNO Voeding bedanken voor het bieden van een mogelijkheid tot het doen van een promotieonderzoek. Het was inspirerend om naast mijn eigen onderzoek ook betrokken te worden bij de toepassing van migratieonderzoek aan verpakkingen in de praktijk.

Heel veel dank aan mijn twee directe begeleiders, Matthijs Dekker en Thomas Hankemeier, voor hulp en steun gedurende het gehele projekt. Matthijs voor talloze discussies over modellen en experimentele aanpak. Thomas voor inspirerende discussies over polymeren en voor zeer deskundige hulp op het gebied van chemische analyses.

Ik wil ook graag mijn promotor Wim Jongen bedanken. Van hem heb ik geleerd om breder te kijken dan alleen naar mijn eigen kleine onderzoeksgebied. Mijn tweede promotor, Hans Wesselingh, is op een afstand bij het projekt betrokken geweest maar is een grote inspiratiebron. De discussies die wij gedurende het projekt hadden hielpen mij om nieuwe ideeën te vormen en verder te gaan met mijn onderzoek.

Graag wil ik ook Jozef Linssen and Pieternel Luning bedanken voor hun bijdrage, met name in het begin van dit projekt.

Rinus Rijk wil ik bedanken voor de uitermate vakbekwame hulp op het gebied van migratieanalyses en wetgeving. Natuurlijk wil ik hem ook bedanken voor leuk gezelschap tijdens onze reisjes naar diverse EG-vergaderingen. I would also like to thank all participants of the European thematic network for migration modelling and of the Recyclability-project for sharing their knowledge with me. Special thanks go to Alexandre Feigenbaum and his colleagues for inviting me to their lab at INRA.

Jacques Sampers en Jos Hennen van DSM Research in Geleen ben ik zeer dankbaar voor het verstrekken van plastic voor mijn experimenten en voor interessante discussies. Ook dank aan Arjan Mank van Philips Research en Kees de Graauw van Universiteit Utrecht voor hulp met LA-ICP-MS respectievelijk CSLM.

Ik wil mijn twee afstudeervakkers, Kirsty and Hanneke, ook graag bedanken voor hun fantastische inzet en goed werk.

Dit onderzoek was niet mogelijk geweest zonder de hulp en gezelligheid van alle medewerkers van de afdeling Verpakking & Sensortechnologie van TNO Voeding. Extra veel dank aan Liliane en Karin die altijd klaar stonden om onder andere de GC te repareren, aan Richard en Yvonne voor hulp met de HPLC en aan Karl, Lieke, Tjoena, Sander en Monique voor het helpen oplossen van andere praktische problemen.

Tot slot wil ik mijn ouders bedanken die mij vanuit Zweden veel steun boden en mij bleven aanmoedigen gedurende de afgelopen jaren. Lieve Chris, dankjewel voor je hulp en steun. Ook jij bent inmiddels een klein beetje een diffusie-expert geworden!

Curriculum Vitae

Ingrid Erika Helmroth werd geboren op 10 oktober 1973 te Arnhem met de zweedse nationaliteit. In 1992 behaalde zij haar VWO-diploma aan het Rhedens Lyceum te Roozendaal. In datzelfde jaar begon zij aan de studie Levensmiddelentechnologie aan de Landbouwuniversiteit te Wageningen, waarin ze zich specialiseerde in de richting proceskunde. Als onderdeel van haar studie deed zij een 5-maands afstudeervak bij zowel de vakgroep Proceskunde als Geïntegreerde Levensmiddelentechnologie. Ook liep ze stage bij het Institut für Lebensmittelwissenschaften aan de ETH te Zürich, Zwitserland, en bij Tetra Pak R&D te Lund, Zweden. In 1997 studeerde zij af. Na haar studie werkte zij 3 maanden als uitzendkracht bij de afdeling Verpakkingen van TNO Voeding te Zeist. Begin 1998 is ze op dezelfde afdeling begonnen als AiO aan een promotieonderzoek waarvan het resultaat is weergegeven in dit proefschrift.

Paranimfen: Liliane Strijk en Annika Envall