Direct Measurement of Additive Migration from Low-Density Polyethylene as a Function of Space and Time

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ABSTRACT: A method, based on microtoming and GC analysis, for studying migration of additives inside polymers as a function of space and time was validated for Irganox 1076 migrating from low-density polyethylene to ethanol. The consistency of the mass balance of the total amount of Irganox 1076 in the polymer and the solvent after different incubation times was acceptable considering errors introduced by the analytical procedure. A solution of Fick diffusion equations, fitted to concentration profiles inside the polymer at different incubation times, was found to describe well the transport process as a function of both position and time with a diffusion coefficient of 1.1×10^{-13} $m^2\ s^{-1}$. This value corresponded to the diffusion coefficient obtained using conventional measurements of an Irganox 1076 concentration in ethanol as a function of time. Compared to a stationary solvent, no significant effect was observed on the diffusion coefficient by gently shaking the ethanol. Diffusion coefficients measured at different temperatures using the validated method followed an Arrhenius type of relationship with an activation energy of 113 kJ mol^{-1}. Conclusively, the method was found to be well suitable for studying additive migration in polymers as a function of both space and time. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3185–3190, 2002

Key words: polyethylene (PE); additives; diffusion

INTRODUCTION

The migration of additives from plastics to food products or pharmaceuticals is an important problem in packaging technology. In spite of extensive research in this area, there is still a lack of understanding about the migration of large molecules (>200 g/mol) from a polymer matrix to a contacting solvent. Current migration research focuses mainly on the measurement of the 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 that are used to describe the transport of molecules through polymers, are, in general, partial differential equations in terms of both time and space and are therefore best studied as such when insight in the transport process is required. However, not many articles deal with the direct measurement of the local additive concentration in polymers, despite the advantage of obtaining information about the migration process as a function of both time and space. Slicing the polymer with a microtome has been shown to give some promising results,[1–4] but the method still lacks satisfactory validation. Besides the purpose of studying complex migration processes, a proper evaluation of the method is also important as microtoming may be used to validate new and promising concentration profiling techniques such as confocal microscopy,[5,6] Raman microscopy,[7] and NMR.[8–10]

The aim of this article was to validate a method based on microtoming and GC analysis for studying transport processes 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 the 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 the polymer and solvent. The total amount of Irganox 1076 in the polymer and solvent should, at all time instances, 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] that are known to describe the transport of Irganox 1076 from LDPE to ethanol.[17]

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THEORY

Mass balance equation

The mass balance may be written as

$$M_{P,initial} = M_{P,t} + M_{S,t} \quad (1)$$

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

Diffusion equation

The migration process in a polymer slab may be described by the second diffusion equation of Fick for unidirectional transport[15]:

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

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

$$C_P(x,0) = C_0 \quad (3)$$

$$C_S(0) = 0 \quad (4)$$

Boundary condition:

$$C_P(0,t) = C_P(L,t) = C_S(t) \quad (5)$$

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

The solution of eq. (2) using eqs. (3)–(5) is based on the following assumptions:

1. Initially, the additive is homogeneously distributed throughout the polymer.
2. For the used polymer/additive/solvent combination and temperature, the diffusion coefficient (D) is constant. Effects due to penetration of the solvent into the polymer may be ignored due to the low interaction between LDPE (δ = 16.96 MPa½) and ethanol (δ = 26.0 MPa½).[19] As the Irganox 1076 concentration in the polymer is low (<0.4%), concentration effects of Irganox 1076 itself may also be ignored.
3. There is no concentration gradient in the solvent, as diffusion through the polymer is much slower than is 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 additive concentrations at both sides of the interface between the polymer and the solvent are equal, according to a partition coefficient (ratio of additive concentrations in polymer and solvent) of 1. This is justified as the solubility of Irganox 1076 in ethanol is good. In practice, as the solvent volume is large with respect to the polymer volume, the solvent concentration will always be almost equal to zero. Mathematically, the concentration in the polymer at the interface is assumed to be equal to the concentration in the solvent at one time-step earlier. This assumption is justified as long as the step size in time is very small. The concentration in the solvent was calculated using the mass balance eq. (1).

EXPERIMENTAL

LDPE slabs, prepared by compression molding, with a thickness of 1.6 mm and 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), MW = 531 g mol^{-1}] were especially 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 cease the migration process. A piece of 1.2 cm^2 was cut 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 preweighed vials and the exact weight of the polymer per vial (hereafter considered as one slice) was determined. The slices were extracted overnight with isooctane at 40°C, after which an internal standard (hexadecyl-3,5-di-*tert*-butyl-4-hydroxybenzoate, Aldrich, Zwijndrecht, the Netherlands) was added. The extracts were analyzed 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

TABLE I
Mass Balance of Irganox 1076 in Polymer and Solvent Standardized to a Polymer Mass of 1 g
[Symbols as Explained in Eq. (1)]

t (min)	M_P (mg)[a]	M_S (mg)[b]	$M_P + M_S$ (mg)	Deviation from $M_{initial}$ (%)[c]
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
14,400	2.13	1.63	3.76	5.0
25,920	1.56	2.13	3.69	3.1

[a] Sum of the amount in all slices of half the polymer slab piece multiplied by two.
[b] Interpolated values of curve of Irganox 1076 concentration in ethanol as a function of time.
[c] Deviation calculated as $[(M_P + M_S) - M_{initial}]M_{initial} \times 100$.

retention gap (deactivated with OV-1701-OH, BGB Analytik, Anwil, Switzerland). In case the concentration was below the detection limit (0.1 mg L^{-1}), the extracts were concentrated by evaporation under nitrogen.

The position along the thickness of the slab was calculated by

$$x_j = \frac{1}{\rho A}\left(\sum_{i=1}^{j} M_i - \frac{1}{2} M_j\right) \quad (6)$$

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

Determination of the Irganox 1076 concentration in ethanol as a function of time was carried out as described earlier,[17] with the exception that the polymer slab pieces were fully immersed in the ethanol, instead of single-sided exposure. In short, a preweighed polymer slab piece of the same LDPE as used for the concentration profile experiments (also 4 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.

RESULTS AND DISCUSSION

The mass balance given by eq. (1) for Irganox 1076 in the polymer and solvent after different incubation times is presented in Table I. The total amount of Irganox 1076 in each polymer slab piece was obtained

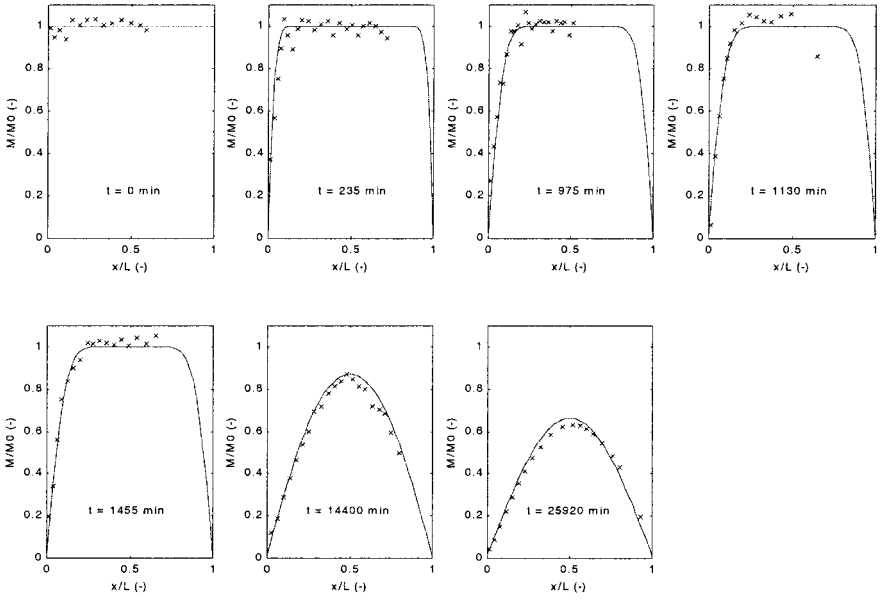

Figure 1 Concentration profiles of Irganox 1076 in LDPE for seven different incubation times expressed as the amount in the polymer at time t relative to the initial amount in the polymer per unit polymer weight. Experimental data are shown by crosses and the best-fitting curve by solid lines.

TABLE II
Diffusion Coefficients from Individual Fits of the Concentration Profile in the Polymer at Each Incubation Time

t (min)	D ($m^2\ s^{-1}$) $\times 10^{14}$
235	14
975	8.4
1130	9.8
1455	9.0
14,400	12
25,920	12

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). The 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 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. One cause of the fact that the deviation in all cases was slightly positive 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 1(a–g) shows the experimental data of seven incubation times at 40°C together with the best-fitting physical model given by eq. (2) using the least-square error criterion[18] for all observations simultaneously. Figure 1(a) confirms that the additive initially was 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} (SD = 0.11 mg g^{-1}, $n = 14$). In general, the model fits the experimental data quite well throughout the whole process. The obtained diffusion coefficient was 1.1×10^{-13} $m^2\ s^{-1}$. Table II shows the diffusion coefficients obtained from individual fits of the concentration profile of each incubation time. The average of these diffusion coefficients is 1.1×10^{-13} $m^2\ s^{-1}$, which corresponds well with the diffusion coefficient obtained by fitting all profiles simultaneously. 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. At short times, Irganox 1076 has only migrated from x positions near the contacting surface, resulting in few points contributing to the estimation of the diffusion coefficient. Therefore, in case the concentration profiles, in practice, cannot be determined during the whole migration process, the diffusion coefficient is best estimated using longer incubation times.

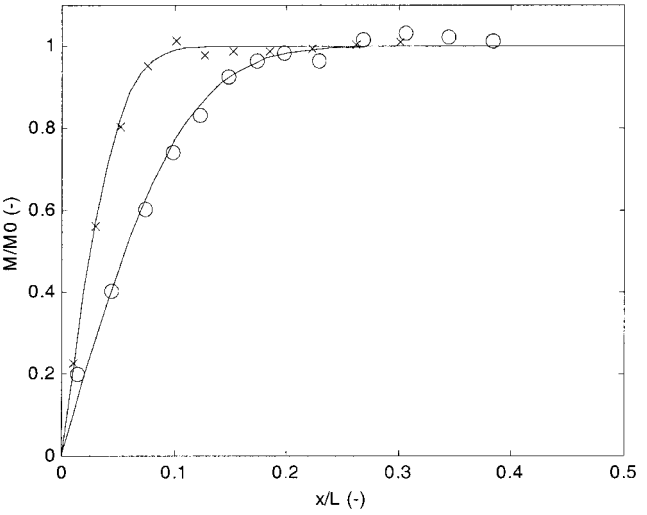

Figure 2 Concentration profiles of Irganox 1076 in LDPE in contact with ethanol after an incubation time of (×) $t = 235$ min and (○) $t = 1130$ min under gentle shaking, expressed as the amount in the polymer at time t relative to the initial amount in the polymer per unit polymer weight. The best-fitting curve is shown by solid lines.

Assumption 3 (there is no concentration gradient in the solvent) was checked specifically by measuring two concentration profiles after incubation under gentle shaking of the solvent. Figure 2 shows the concentration profiles inside the polymer and the best-fitting curve after 235 and 1130 min of incubation in ethanol under gentle shaking (80 rotations/min) in a water bath of 40°C. The obtained diffusion coefficient was 1.3×10^{-13} $m^2\ s^{-1}$, which is not significantly different

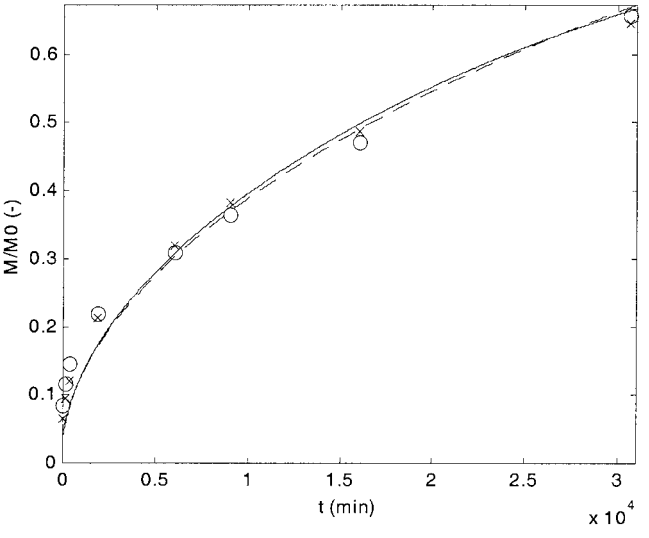

Figure 3 Migration of Irganox 1076 from LDPE into ethanol as a function of time expressed as the amount in the solvent at time t relative to the initial amount in the polymer per unit polymer weight. Experimental data (×,○) of the duplicate measurements and (solid and dotted lines) of the best-fitting curves.

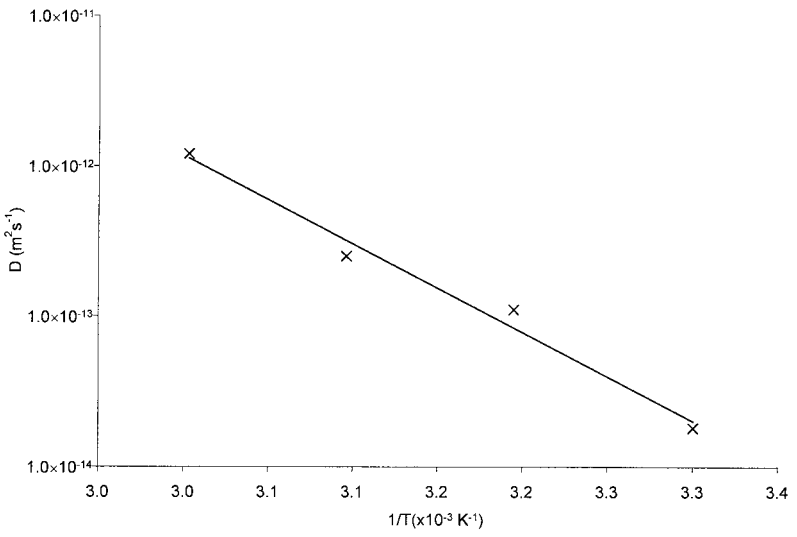

Figure 4 Diffusion coefficient of Irganox 1076 in LDPE in contact with ethanol as a function of temperature. Calculations were performed on concentration profiles of 20 h at 30°C, 18 h at 50°C, and 16 h at 60°C. At 40°C, the concentration profiles from Figure 1 were used.

from the diffusion coefficient obtained for the process with stationary ethanol ($D = 1.1 \times 10^{-13}$ 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 the diffusion coefficients obtained from conventional measurements of the 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 3 together with the best-fitting curve given by eq. (2) according to the least-square error criterion. At short incubation times, the model predictions are somewhat lower than are 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. This, as mentioned earlier, also explains some of the positive deviation found in the mass-balance calculations. The obtained diffusion coefficients 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 ($D = 1.1 \times 10^{-13}$ m^2 s^{-1}).

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

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right) \quad (7)$$

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 preexponential factor (m^2 s^{-1}). Figure 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 was 113 kJ mol^{-1}, which corresponds 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]

CONCLUSIONS

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

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