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► **To cite this version:**

Patrice Dole, Ioannis S Voulzatis, Olivier Vitrac, Susana Aucejo, Alain Reynier, et al.. Modelling of migration from multilayers and functional barriers: estimation of parameters. *Food Additives and Contaminants*, 2006, 23 (10), pp.1038-1052. 10.1080/02652030600658003 . hal-00577597

HAL Id: hal-00577597

<https://hal.science/hal-00577597>

Submitted on 17 Mar 2011

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Modelling of migration from multilayers and functional barriers: estimation of parameters

Journal:	<i>Food Additives and Contaminants</i>
Manuscript ID:	TFAC-2005-303.R1
Manuscript Type:	Original Research Paper
Date Submitted by the Author:	22-Feb-2006
Complete List of Authors:	DOLE, Patrice; INRA, UMR FARE Voultzatis, Ioannis; INRA, UMR FARE Vitrac, Olivier; INRA, UMR FARE AUCEJO, Susana; TNO, Analytical Science REYNIER, Alain; INRA, UMR FARE HANKEMAIER, Thomas; TNO, ANALYTICAL SCIENCES FEIGENBAUM, Alexandre; INRA, UMR FARE
Methods/Techniques:	GC, Risk assessment - modelling
Additives/Contaminants:	Migration - diffusion, Food contact materials, Packaging recycling, Packaging - migration modelling
Food Types:	

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6 **Modelling of migration from multi-layers and functional barriers:**
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8 **estimation of parameters**
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14 Patrice Dole^a, Yiannis Voulzatis^a, Olivier Vitrac^a, Alain Reynier^a, Thomas
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30 **KEYWORDS**
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34 Food packaging, migration, recycling, functional barrier, modelling, safety
35 assessment
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ABSTRACT

Functional barriers form parts of multilayer packaging materials, deemed to protect the food from migration of a broad range of contaminants e.g. associated with reused packaging. Often, neither the presence nor the identity of the contaminants is known, so that safety assessment of the materials has to rely on predictive tools. Several complementary freeware described here allow one to model diffusion in multi-layer films. These tools require the input of parameters which are not easy to determine or to predict. Previous work has focused on prediction of diffusion coefficients at temperatures of storage of packaging in contact with food. However many other kinetic and thermodynamic parameters are needed to describe transport properties during processing of material at high temperature and during its shelf life. All parameters needed for the calculations are discussed. In order to propose default values, the approach consists of (i) reviewing available literature data (ii) running experiments on polypropylene, polyethylene and poly(ethylene vinyl alcohol) in typical conditions (separately diffusion during processing and migration) (iii) simulating numerical sets for typical situations. Several freeware are proposed to simulate migration from multi-layers and functional barriers using the default parameters.

INTRODUCTION

Functional barriers are used in packaging to protect food from the migration of accidental contaminants from recycled polymers. The presence of a virgin barrier layer between recycled polymer and food, delays the beginning of migration kinetics; this time delay is called lag time. The evaluation of barrier performances of a material towards a given packaging application requires (i) determination of whether contamination of the barrier occurs during processing of the multi-layer material (Pennarun et al 2004a, Franz et al 1997, Perou et al 1997) and (ii) determination as to whether the lag time for migration is lower than the shelf life of the packaging (Widen et al 2004, Pennarun et al 2005, Franz et al 1997)

As the mass transport phenomena during processing and during food contact are mainly controlled by diffusion effects, the general strategy of the food packaging scientific community was to accumulate diffusion coefficient reference data (i) at molten state for processing conditions (Pennarun *et al* 2004a), and (ii) at 40°C for food contact conditions (Dole *et al* , Pennarun *et al* 2004b, 2004c, Simal-Gandara *et al* 2000a, 2000b); these data, focused on low molecular weight migrants were used to complete the Piringer data bases and equations involving a large molecular weight range (Baner *et al* 1996, Begley *et al* 2005).

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4 However migration is obviously not controlled only by diffusion, but also by
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6 partition coefficients, heat transfer, heat diffusion, mass transfer, diffusion
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8 coefficient activation (Dole *et al.* 2006), and factors describing the effect of
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10 plasticization on diffusion (Reynier *et al.* 2002). This paper addresses
11
12 systematically each of these factors.

- 13
14 - Transport properties (matter and heat) during processing of the materials are
15
16 investigated by monitoring a UV absorbing probe in the thickness of melted
17
18 polymers. The parameters to be used for prediction of diffusion during
19
20 processing are discussed with the background of literature data.
21
22 - Transport properties during migration step are investigated by monitoring
23
24 migration of surrogates (model contaminants) from samples obtained by
25
26 minimizing contamination at molten state. The parameters to be used for
27
28 prediction of diffusion are discussed on the basis of literature data. Interface
29
30 effects (partition and mass transfer) are discussed on the basis of numerical
31
32 simulations of sets of typical situations.
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35 The numerical tools for simulations and interpretation of experimental data were
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37 developed in the frame of this work. They are available as freeware.
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MATERIALS and METHODS

Materials and surrogates

* EVOH, HDPE and PP were supplied by Cryovac (Passirana di Rho, IT).

Model contaminants (surrogates) were chosen from the FDA and ILSI proposals (ILSI 1998). 2,5-dimethoxyacetophenone (DMA) was added as a UV marker. The final list was: Trichloroethane (Merck), toluene (Merck), chlorobenzene (Fluka), phenylcyclohexane (Merck), benzophenone (Merck), methyl margarinate (Merck), and dimethoxyacetophenone (Aldrich).

EVOH resin was impregnated with DMA according to a described procedure (Pennarun *et al.* 2004a).

* The impregnation of polypropylene (PP) and high density polyethylene (HDPE) both with volatile and with non-volatile surrogates was made according to a dedicated procedure (Papaspirides *et al.*, 2005).

Measurement of DMA diffusion profiles after three-layer processing using UV microspectrophotometry

An [(ethylene – vinyl alcohol) copolymer] (EVOH) three-layer film was processed with an industrial extruder (CRYOVAC, US) at 210°C. The inner layer was spiked with 2,5-dimethoxyacetophenone (DMA). After co-extrusion the

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4 sample was stored below 0°C to prevent further diffusion. 30 µm microtomic
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6 cross sections were then analyzed with a UV microspectrophotometer (Carl Zeiss
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8 UV-visible spectrophotometer equipped with a Xenon lamp and a microscope unit
9
10 for analysis of small areas). The analysed area is a circle with radius 1 µm. The
11
12 concentration gradient of DMA is recorded from the maximum absorption peak of
13
14 DMA at 330 nm (Pennarun *et al.* 2004a).

15 16 17 18 ***Measurement of diffusion coefficients at 40°C***

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20 A diffusion test in a stack of films is realized according to a procedure described by
21
22 Reynier (2001a and b).
23
24

25 26 27 ***Migration testing***

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29 The migration tests are made with a three-layer film in contact with a simulant.
30
31 Several three-layer film samples (virgin/contaminated/virgin layers, noted V/C/V)
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33 are prepared by co-extrusion, using a specially design of the co-extruder, in order
34
35 to minimize contact time between layers at molten state. For that purpose, a
36
37 Scamex (Crosnes, France) micro-extruder was equipped with a short slit die. A
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39 calander was placed at 1 cm after the co-extrusion die, which also contributed to
40
41 minimize the cooling time. Samples were rapidly cooled at -30°C just after
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43 extrusion to prevent further diffusion. Migration tests were started few hours after
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45 this processing operation. Samples with homogeneous thickness were selected,
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47 and stored at -80°C to prevent losses of surrogates by evaporation and diffusion
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4 before the start of the migration experiments, Samples were then placed in
5 migration cells filled with the simulant (water, ethanol, or olive oil). The cells are
6 stored at a controlled temperature (40°C) and the surrogates diffuse through the
7 virgin polymer layer into the simulant (Figure 1). The cells are glass vials, and the
8 sample is fitted in the cap. A different cell is used for each individual
9 measurement. The concentration of migrating surrogates is determined at different
10 times by analysing the simulant. In order to take into account potential variations
11 of initial concentrations in the film, it is important to analyse also the three-layer
12 film at the end of the migration test: the initial concentration is equal to [migrated
13 quantity + quantity remaining in film, determined by extraction at the end of the
14 test].
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28 Kinetics displayed are expressed in function of $(t/L^2)^{0.5}$ in order to take into
29 account local variations of the thickness from sample to sample. The thickness of
30 each sample was measured by visible microscopy.
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36 THEORETICAL BACKGROUND

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40 As long as the external surface remains free of contaminants, mass transport within the
41 functional barrier is similar to that in a system with a semi-infinite geometry (no
42 boundary effects). But when contaminants reach the interface with food, the different
43 affinities of the contaminant with the food and with the polymer are responsible for a
44 discontinuity of the concentration profile. The jump in concentration profiles is
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commonly described by assuming an instantaneous and local thermodynamic equilibrium between both sides of the surface, corresponding to a control by a partition coefficient (assuming a linear desorption isotherm).

Migration is obviously negligible as long as the probability of migration of a molecule is statistically “zero”. This is the case e.g. when the averaged migration time required by a single molecule to reach the external surface through the functional barrier (distance fb) is larger than the life time (t) of the packaging material [which is the sum of the times of processing, of storage of the empty package and of shelf life of the packaged food]. In literature, the critical migration time, following which the cumulative flux crossing the external surface can not be longer considered to be zero is calculated in several ways (Feigenbaum *et al.* 2005).

For longer contact times, the contamination of the contact surface is significant and previous approximations (either semi-infinite media or impervious boundary condition) are no longer valid. The mass transport description must take into account phenomena at the food-packaging boundary. The uni-directional and dimensionless mass transport with a constant and uniform diffusion coefficient, D , in the packaging material is described by equation (1):

$$\frac{\partial u}{\partial Fo} = \frac{\partial^2 u}{\partial x^{*2}} \quad \text{with } 0 \leq x^* \leq 1 \quad (1)$$

where $u_{(x^*, Fo)} = \frac{L}{L - fb} \frac{C_p^{(x,t)}}{C_{p,0}}$, $Fo = \frac{D \cdot t}{4 \cdot L^2}$ and $x^* = \frac{x}{2 \cdot L}$ are respectively the dimensionless concentration (or equivalent to a Brownian density in the packaging material), time and

position. $C_{P,0}$ is the initial concentration in the contaminated material (expressed in kg of contaminant per kg of contaminated material), which is assumed to be homogeneous.

The functional barrier is assumed to be initially non-contaminated, symmetric and located at positions $x_f^* = fb/(2 \cdot L)$ and $1 - x_f^*$. The initial concentration profile is

consequently $u_{(-x_f^* \leq x^* \leq +x_f^*, Fo=0)} = \frac{L}{L - fb}$ and 0 elsewhere.

Only one side ($x^*=1$) is assumed to be contact with food. The opposite side at $x^*=0$ is assumed to be impervious:

$$\left. \frac{\partial u}{\partial x^*} \right|_{x^*=0} = 0 \quad (2)$$

For liquid and semi-liquid foods, the boundary condition on food side ($x^*=1$) assumes a pervious contact, controlled by a partition coefficient between food and packaging,

$K_{FP} = \frac{v|_{x \rightarrow 1^+}}{u|_{x \rightarrow 1^-}}$ with v the dimensionless concentration in food, and a mass transfer coefficient, h , given by equation (3):

$$j^* = \frac{2L}{D \cdot C_{P,0}} j = - \left. \frac{\partial u}{\partial x^*} \right|_{x^*=1} = Bi \cdot K_{FP} \cdot \left(u|_{x^*=1} - \frac{\bar{v}}{K_{FP}} \right) \quad (3)$$

where j and j^* are respectively the mass flux and the dimensionless mass flux.

$Bi = \frac{h \cdot l}{D}$ is the mass Biot number which represents the ratio between the internal and external resistances to mass transfer.

In a solid, the number is low. In liquids, it is much larger than 1.

\bar{v} is the averaged dimensionless concentration in food and is inferred from a macroscopic mass balance between food and the packaging material. If the food is not initially contaminated, one gets equation (4):

$$\bar{u} + \int_0^{F_0} j^*(\tau) \cdot d\tau = \bar{u} + \frac{\bar{v}}{L_{PF}} = 1 \quad (4)$$

with $\bar{u} = \int_0^1 u(x^*, F_0) \cdot dx^*$ and $L_{PF} = \frac{V_P \cdot \rho_P}{V_F \cdot \rho_F}$, where V_i and ρ_i are respectively the volume and the density of the phase $i=P,F$ (P =packaging material, F =Food).

Finally, the concentration in food C_F , expressed in mass of migrant per mass of food is given by equation (5):

$$C_F^{(F_0)} = C_{P,0} \cdot \left(1 - \frac{bf}{L}\right) \cdot L_{PF} \cdot \bar{v} \quad (5)$$

The migration rate into food is increased when the partition coefficient favours transfer into food, and when the mass transport within the food is not limiting. The worst case scenario corresponds to a zero value at the food / polymer interface, on the polymer side during the whole process (i.e. no local accumulation on the polymer side). The migration rate into the food is then controlled only by the diffusion of contaminants through the contaminated region and the functional barrier. The latter situation implies replacement of the boundary equation defined by equation (3) by equation (6):

$$u(x^* = 1, F_0) = 0 \quad (6)$$

It must be emphasized that if partition effects are significant with large Bi values (i.e. >100), differentiation of equation (4) with time for $u|_{x^*=1} = \frac{\bar{v}}{K}$ leads to the following boundary condition:

$$\frac{\partial u}{\partial F_0} \Big|_{x^*=1} = \frac{L_{PF}}{K_{FP}} j^* = - \frac{L_{PF}}{K_{FP}} \frac{\partial u}{\partial x^*} \Big|_{x^*=1} \quad (7)$$

In the software Multiwise and in the following of this paper, Bi will be identified as H.

PRACTICAL MODELLING OF MASS TRANSPORT

Variables and input parameters

KF/P = partition coefficient between Food and Polymer or between liquid simulant and polymer

Hl/p = mass transport coefficient at the food /polymer interface

Hp/a = mass transport coefficient at the polymer / air interface

Hl/p → 0, high resistance to mass transfer at polymer/food interface

Hl/p → ∞ no resistance to mass transfer at interface, worst case situation

B = swelling factor (B=0: no plasticization effect)

C0 = CP,0 = Initial concentration of the contaminant in the recycled layer

Cfb,t = concentration of the contaminant on the external surface at time

fb (μm) = thickness of functional barrier (In the PROCESS software, only fb/L = 0.33 is currently available)

L (μm) = thickness of the whole material

hc [W m⁻² s⁻¹] = heat transfer coefficient (cooling after assembling layers during process). In the Multitemp freeware, a parameter H is used H [cm² s⁻¹] = (Cp * hc)/ρ.

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4 hc = 10: natural cooling by convection in air

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6 hc = 50: cooling by forced convection in air

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8 hc = 200: cooling by contact with a refrigerated mould wall

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11 As pointed out the diffusion of the contaminant through the functional barrier
12 occurs first during processing (short time but high temperature) and then during
13 storage and finally during use of the material (possibly after hot filling). The two
14 last steps occur around ambient temperatures.

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19 Two coupled software have been developed in order to simulate these successive
20 steps as they occur in real cases: the diffusion profiles (i.e. repartition of the
21 contaminant across the thickness of the multilayer) obtained by simulating
22 diffusion during processing (high temperature: « multitemp ») can be used as
23 starting point of the calculation made by the second software (migration:
24 « multiwise »). It is possible to use these several times, successively, e.g. to
25 simulate diffusion during successive steps like processing at constant temperature,
26 then cooling, then storage of empty package, then hot filling, then migration
27 during storage in contact with food ...

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39 Beta versions of the different software developed for the project can be
40 downloaded as a freeware at: [http://www.inra.fr/Internet/Produits/securite-](http://www.inra.fr/Internet/Produits/securite-emballage/pagefr.html)
41 [emballage/pagefr.html](http://www.inra.fr/Internet/Produits/securite-emballage/pagefr.html). The download link goes to a folder “INRAMIG”, which
42 has to be put under C://. The “.EXE” files are located in an “APP” sub-folder.

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47 Information and assistance are found in a power point file “how to use.pps”.

Mass transport during processing: MULTITEMP software

** Pollution of the barrier layer in the coextruder die or in the coinjection mold*

Diffusion is described by the second Fick's law. The diffusion coefficient is a function of the local temperature at time t . An Arrhenius activation is assumed.

Heat diffusion is described by Fourier's law. Heat transfer coefficients (cm s^{-1}) taken into account are at polymer / mold or polymer / die interface.

** Estimation of the parameters:* diffusion parameters and their thermal activation can be approximated using reference data of a fast diffusing (worst case) surrogate (see discussion below). The first problem is that it is difficult to appreciate the importance of matter losses both in the extruder and during cooling of co-extruded films. These losses are linked to the volatility of the species but also to the geometry of the machines. The "worst case approach" (for the purpose of migration prediction) consists in considering that no losses occur. The second problem is to calculate the temperature gradient across the thickness and as a function of time. This strongly depends on the heat convection parameters (i.e. in fact on the conditions of cooling) and not much on heat diffusion, which can be approximated easily by default parameters for all polymers at molten state.

Simplified tool: PROCESS software

A reduced number of parameters seems relevant for a rough description of diffusion during the process in worst case situations. This leads to simplified software, called PROCESS, taking into account a reduced number of variables,

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4 and describing qualitatively the influence of the range of their variation.
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6 PROCESS considers the type of polymer (described as the diffusion coefficient of
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8 DMA at the melt temperature), the packaging thickness range (both absolute
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10 value of thickness L – from 10 μm to 20 mm - of material and relative thickness
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12 of the functional barrier fb – arbitrarily taken as 33 % in the first version of the
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14 software), the extrusion time (see below), the extrusion temperature and the heat
15
16 transfer coefficient hc (from 10 to 200 $\text{W m}^{-2} \text{s}^{-1}$, considered here as a flux).
17
18 PROCESS considers a residence time in a mould or in a co-extrusion dye at a
19
20 constant temperature, followed by a convective cooling down to room
21
22 temperature, with an overall duration of both stages of 60 s. PROCESS calculates
23
24 abacuses of percentages of concentration of DMA (the model contaminant) of the
25
26 functional barrier (average concentration) and of the external surface (local
27
28 concentration).

29
30 **Assumptions:** mass transport is assumed with impervious boundary conditions,
31
32 and is activated with temperature according to an Arrhenius relation. Heat transfer
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34 is assumed to be purely diffusive and controlled by an apparent diffusion
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36 coefficient constant for all polymers. As a result, source terms are arbitrary
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38 distributed through the whole thickness of the material. Diffusion coefficients and
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40 activation energies (Pennarun 2004a) used are those of DMA. PROCESS does not
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42 calculate the results, but selects them from a data base of pre-calculated situations,
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44 choosing the closest to the problem raised. PROCESS generates almost
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46 instantaneously a result, selected from more than 10 000 different conditions (in
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48 the range of input variables) in the database of simulated results. New results are
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4 either linearly or non linearly (cubic Hermite interpolation) interpolated through a
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6 suitable grid of reference conditions. Simulated results included in the database
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8 are obtained from a rapid ad hoc numerical simulation tool using i) 60 quadratic
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10 non uniform finite elements (adapted to the singularity of the initial concentration
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12 profile) for the discretization in space, ii) a variable order (up to 5) backward
13
14 differences based on Klopfenstein-Shampine family of numerical differentiation
15
16 formulas for time marching.
17

18 19 20 **Migration of contaminants into food: MULTIWISE software**

21 22 * Migrant diffusion

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24 The diffusion is described by the second Fick's law. The diffusion coefficient is a
25
26 function of the local concentration of food constituents (or of the food simulant)
27
28 in the plastic at time t. One diffusion coefficient of a given surrogate is defined for
29
30 each layer in absence of food constituent; its value is allowed to vary with the
31
32 local concentration of the swelling simulant. An exponential relation between D
33
34 and food constituent (simulant) concentration is assumed.

35
36 $D \text{ at } t = \text{initial } D \text{ [entered value]} \times \exp(B \times \text{simulant concentration at } t)$

37
38 The parameter B characterises the swelling effect of the food constituent
39
40 (simulant). When B=0, the diffusion coefficient does not depend on the simulant
41
42 concentration – no “swelling” nor “plasticizing” effect.

43 44 * Influence of Food sorption

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46 Food sorption is described by the second Fick's law. The diffusion coefficient of
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48 food constituents into the polymer is a function of the local food concentration at
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4 time t . An exponential relationship between D_{food} and food concentration is
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6 assumed.

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10 * Mass transfer of contaminant at interfaces:

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12 $H_{P/a}$ and $H_{l/P}$ are the mass transfer coefficients at the polymer /air and at
13
14 the liquid (food) / polymer interfaces. Three different situations are generally
15
16 possible for H ($H_{P/a}$ and $H_{l/P}$) parameters:

17
18 H is equal to zero: no transfer is possible at this interface (e.g. the additive
19
20 not soluble or not volatile, or the external medium is a metallic substrate).

21
22 H is "infinite": the transfer from the interface is instantaneous. As the
23
24 external volume is considered infinite, the concentration on the surface is equal to
25
26 zero.

27
28 $H > 0$ but low: in this case, desorption or migration of the contaminant is
29
30 partly controlled by its rate of evacuation at air or food interfaces.

31
32 Mass transfer coefficients can be assumed equal to zero at the interface with air.

33 34 35 **Simplified tool: Storage software:**

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37 STORAGE simulates the migration of different contaminants from recycled
38
39 plastic films (in symmetrical materials containing a functional barrier) into food
40
41 during contact with food.

42
43 As for PROCESS, STORAGE is based on a database of simulated results. New
44
45 results are either linearly or non linearly (cubic Hermite interpolation)
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47 interpolated through a suitable grid of reference conditions.
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4 Inputs: L (10 μm to 20 mm), fb (5 to 40%), D (10^{-7} to 10^{-14} $\text{cm}^2\cdot\text{s}^{-1}$), t (0 to 730

5
6 days)

7
8 Output: level of migration into food.

9
10 Assumptions: A diffusive mass transport is assumed, with a worst case scenario:

11
12 no external resistance between film and food. A one side contact is assumed.

13
14
15
16 **Note:** in the software available on the web site, for simplification, the hc

17
18 (MULTITEMP), Hl/p (MULTIWISE) parameter are just named H. Hp/a is not

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20 taken into account. Hl/p can be adjusted.

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26 **RESULTS AND DISCUSSIONS**

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30 **A) Diffusion during processing of functional barriers**

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34 An experiment conducted on a plant, with DMA as surrogate, diffusing in a
35
36 multilayer during processing. The DMA distribution displayed in Figure 2 has
37
38 been obtained after processing a [virgin EVOH/EVOH (+DMA)/virgin EVOH]
39
40 80 μm thick three-layer at 210°C.

41
42 Two essential observations can be made: (i) the virgin layer is contaminated and
43
44 (ii) the diffusion has reached the external surface. The slope of the profile near the
45
46 surface suggests an external rate limiting desorption by evaporation.
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4 This profile shape can be simulated by numerical calculation assuming that the
5 diffusion behaviour of EVOH [$D=f(T)$] is a simplified two-step process:

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8 - first, isothermal contact in the extruder die with no possible matter nor heat
9 (both $H = 0$) exchange with the outside of the system;

10
11 - then, a contact between layers during cooling in air (variation of T versus time
12 and space), with the possibility of mass transfer outside the system (evaporation).

13
14 Temperature profiles simulated from (i) classical heat diffusion coefficients of
15 polymers ($1.6 \cdot 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$) (ii) a simplified description of cooling after the
16 extrusion die, assuming no change of state leading to non continuous variation of
17 parameters and constants of diffusion or of heat delivery.
18
19

20
21 Figures 3 and 4 correspond to profiles calculated to simulate the experimental
22 data of Figure 2, with the assumption that with $H/P=0.001$ (fast evaporation) and
23 $H/P=0 \text{ m s}^{-1}$ (no evaporation) respectively. These profiles look very different.
24
25 The corresponding migration kinetics resulting from these materials should be
26 different, but in both cases, the lag times should be equal to zero.
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28

29
30 However, the possibility to fit these specific data as in Figure 3 should not be
31 considered as a validation of a model, since the concentration 0 at the polymer /
32 air interface as well as the profile shape suggest that an important evaporation has
33 taken place. Modelling of evaporation would involve too many parameters, most
34 of them being difficult to evaluate, such as the average (in the considered
35 temperature range) rate of evaporation at the surface, the temperature profiles...
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39 This is why the overestimation method should in first instance be used as an
40 indicative tool to decide whether a pollution of the barrier layer is likely or not to
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4 occur during processing. This should be sufficient to describe most practical
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6 situations, which are expected to be close to either of the two extreme situations:

7
8 - When there is no significant pollution of the barrier during processing, the
9
10 migration step can be calculated independently assuming no pollution at all
11
12 (vertical profiles). With PET, it has been shown experimentally that the pollution
13
14 of a functional barrier of a bottle is negligible during processing (Pennarun *et al.*
15
16 2004a).

17
18 - When the pollution of the barrier is important, no further calculations are
19
20 necessary, the barrier is not efficient, and, as far as a quick decision must be
21
22 taken, the system should not be used as a functional barrier.

23
24 However, in intermediate situations, or to define acceptable conditions of use, it is
25
26 necessary to simulate the process, which requires a good knowledge of the system
27
28 studied, in terms of heat exchange especially.

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32 If the main criteria for safety assessment of a material depend on whether the
33
34 contaminant has reached the surface in contact with the food (see the discussion
35
36 on lag time), it is possible to use a simplified description of the process,
37
38 neglecting evaporation of the surrogates:

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40 - if the barrier is efficient during processing, surface phenomena have no
41
42 influence on the migration, since the migrant has not reached the interface after
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44 processing

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46 - if the barrier is not efficient, no further calculations are necessary.
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4 **Selection of functional barrier materials on the basis of behaviour during**
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6 **processing**
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8 The simplified description used in PROCESS allows classifying the polymers in
9 function of their diffusion behaviour at their melt temperature.

10 The thickness needed to maintain $C_{fb} \leq 0.05 C_0$, at different processing
11 temperatures was calculated for all the polymers in the data base of PROCESS.

12 These times should not be considered as absolute values, as they are calculated in
13 extremely worst case: the diffusion coefficients used are those of DMA. $h_c = 255$
14 $W m^{-2} s^{-1}$, relative functional barrier thickness is 1/3 of the whole material, and
15 the process time $t_e = 0.1$ s. This time is of course not realistic and is used only as
16 reference value for the classification. On Figure 5, each label mentions polymer
17 type and processing temperature. Based on the behaviour of DMA, polymers
18 which are glassy at room temperature are by far the best diffusion barriers.
19

20 PET, PVC, PAN, PVDC, EVOH, PA > PS > Polyolefins, EVA
21

22 Figure 5 allows interpretations like: "a 50 μm PVDC functional barrier is
23 equivalent to 10 000 μm LLDPE".
24

25 The classification thus obtained corresponds roughly to the efficiency of gas
26 barrier polymers: the higher is the glass temperature, the better is the barrier.
27 Again, since this scale is based on the behaviour of DMA, it may take into
28 account specific interactions of this surrogate with the polymer.
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4 **Which parameters can be used for prediction of diffusion during processing?**
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6 For prediction purpose, four parameters are essential: D , h_c , E_a and HP/a . Let us
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8 examine these parameters one by one.
9

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11
12 ***What about D and E_a during processing?***
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14 In the software, the diffusion coefficient and the activation energy used are those
15 of DMA, the reference compound. This is probably a worst case, as DMA has a
16 low molecular weight: low molecular weight substances have high diffusion
17 coefficients and low activation energies (Dole *et al.* 2006). In case of recycling,
18 where the identity of the possible contaminant is unknown, one should take into
19 account such worst case, lower molecular weight reference compounds. This
20 should not lead to major differences as the dependence of D with molecular
21 weight is expected to be low at high temperature (Dole *et al.* 2006). However it
22 would be interesting to have D and E_a data available for several reference
23 compounds, with different chemical groups, in order to better take into account
24 possible specific [diffusant – polymer] interactions. The activation energies
25 measured for DMA in melted polymers were up to 110 kJ/mole in
26 polyacrylonitrile (Pennarun *et al.* 2004a). Since the worst case corresponds to the
27 lowest value (slightest decrease of D during cooling), more information should be
28 obtained in this field. When using the MULTITEMP software to describe the
29 diffusion of an unknown contaminant, a default value of 50 kJ/mole is
30 recommended for diffusion in melted state.
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4 ***What about hc?***
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6 The larger is hc, the quicker is the cooling and the steeper is the decrease of D
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8 once the layers are assembled. In the case of PET co-injection, different scenarios,
9
10 corresponding to basically different cooling conditions, were envisaged. Typical
11
12 values:

13 $hc = 255 \text{ W m}^{-2} \text{ s}^{-1}$: describes cooling of a mould with water at 8°C;

14 $hc = 100 \text{ W m}^{-2} \text{ s}^{-1}$: cooling in an air stream;

15 $hc = 10 \text{ W m}^{-2} \text{ s}^{-1}$: cooling by natural convection of air
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19 The worst case situation in all cases would be $hc = 0 \text{ W m}^{-2} \text{ s}^{-1}$. But this has no
20
21 meaning, as the polymer would not be allowed to cool.
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23 hc values have therefore to be measured in a process, which can be achieved with
24
25 an infrared camera, by following surface – temperature kinetics.
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30 ***What about Hp/a?***
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32 If evaporation takes place during processing (large Hp/a), the average and the
33
34 surface concentration of the contaminant (and consequently its migration) will be
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36 lower (see figure 2), which contributes to the consumer's safety. The current
37
38 version of MULTITEMP however describes processing in a mold, which is a
39
40 worst case situation ($Hp/a = 0$, no evaporation). The future version will include
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42 this variable. Hp/a values can be determined according to Vergnaud (1991).
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48 **B) Migration through functional barriers**
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6 The aim of this part of the work is to establish whether the simplified model
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8 MULTIWISE, with a simple set of default parameters, assuming complete
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10 migration at equilibrium and no rate limiting mass transfers, can describe the
11
12 initial part of migration kinetics. The early stages of migration are the most
13
14 critical in terms of risk assessment of the capacity of a functional barrier to protect
15
16 a food.
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20 The first step was to measure intrinsic diffusion coefficients of the surrogates in
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22 the polymer, i.e. values which could be considered as true values, not apparent
23
24 values. This required tests conducted in absence of liquid simulants, which often
25
26 plasticize the polymers. The Moisan test is well adapted to this requirement (table
27
28 1).
29

30 The second step was to apply the simplified model to fit experimental migration
31
32 kinetics from three-layer materials (prepared with the contaminated layer as
33
34 middle layer) into olive oil and ethanol. The experiments were run for a complete
35
36 set of surrogates in PP and in HDPE. Kinetics are shown for HDPE in Figure 6.
37
38 The experiments were carefully designed, as follows: (i) PP and HDPE, which are
39
40 poor barriers, were used in order to have quick results (ii) the total thickness
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42 (about 300 μm) was adjusted to have a lag time of several hours. Use of a micro-
43
44 extruder allowed minimising the diffusion in the molten state, due to a very short
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46 contact time at high temperature; moreover a calander was placed at 1 cm after
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48 the co-extrusion die, which also contributed to minimize diffusion during the
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4 cooling time. It could thus be assumed that no diffusion occurred during the
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6 processing step. In order to have also no diffusion between date of processing and
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8 date of start of migration tests, the samples were stored at -30 °C immediately
9
10 after their processing.
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14 Intrinsic (in HDPE films) and apparent (into simulants) diffusion coefficients
15
16 were determined from Moisan tests and for migration (from HDPE three-layers
17
18 into ethanol and olive oil) experiments respectively (Table 1). Fits of
19
20 experimental results were made with MULTIWISE, assuming very large values
21
22 of $H/P = 1$ (equivalent to H/P tends to ∞). These D values all lie in the same
23
24 order of magnitude, which suggests that the approach should be further
25
26 simplified, and that swelling effects by the food could be neglected.
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30 On the other hand, it may seem surprising at first glance that apparent diffusion
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32 coefficients with olive oil are not higher than intrinsic ones, and that plasticization
33
34 of the functional barrier does not play a role. This apparent contradiction can be
35
36 solved by considering general knowledge on plasticization: all surrogates in this
37
38 experiment are low molecular weight species (the low molecular weight was one
39
40 of the criteria for the selection of surrogates), which are less influenced by
41
42 plasticization than higher molecular weight compounds, like normal additives
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44 (Reynier *et al.* 2002).
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4 Results for (PP/contaminated PP/PP, not displayed here) three-layer materials
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6 (intrinsic D without solvent, and apparent D with ethanol and with olive oil) show
7
8 a similar situation: the lag times obtained for the migration of the low molecular
9
10 surrogates into both simulants are very close and they can be predicted from
11
12 “intrinsic” diffusion coefficients.
13

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16 Migration of trichloroethane from PP/PP-surrogate/PP three-layers into water
17
18 leads to a different behaviour. Experimental lag times in water are larger than
19
20 with ethanol and with olive oil (compare Figure 6 and Figure 7). Similar results
21
22 are obtained for all the other hydrophobic surrogates, like toluene and
23
24 chlorobenzene. As we have seen above, this cannot be attributed to plasticization.
25
26 Considering the partition coefficient of these hydrophobic surrogates does not
27
28 explain such changes in lag time values. We therefore investigated the possible
29
30 role of the rate limiting mass transfer (HI/P) parameter on the migration of these
31
32 lipophilic surrogates from a lipophilic polymer into water. A simulation of
33
34 migration was made using MULTIWISE, assuming a three-layer structure, and
35
36 different HI/P values: 10^{-11} , 10^{-10} , 10^{-9} , 10^{-8} and 1 ($HI/P \rightarrow \infty$) cm s^{-1} (figure
37
38 8). It appears that there is a considerable effect on lag time.
39

40
41 By contrast, benzophenone, which has more affinity to the aqueous acidic
42
43 simulant, has a lag time identical in the three simulants tested (Figure 9). It seems
44
45 that when there are no rate limiting mass transfer effects, the lag times are
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47 identical and depend mainly on diffusion effects. Despite the considerable work in
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4 literature on migration, there is still little information about such interface effects.
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6 The rate limiting mass transfer parameter (called “convection factor” by
7
8 Vergnaud) (Vergnaud 1991) is usually considered to depend mainly on the liquid
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10 in contact (food or food simulant). Our results suggest that H/P could also
11
12 strongly depend on the structure of the migrant, which requires further exploration
13
14 (Mougharbel *et al.* submitted).
15

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18 **Prediction of migration kinetics: which values are to be used for the**
19
20 **calculations?**
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24 ***What about D in storage conditions?***

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26 Diffusion coefficients at ambient temperature can be approximated using
27
28 reference data obtained with fast diffusing, low molecular weight probes tabulated
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30 for 14 polymers (Dole *et al.* 2006, Feigenbaum *et al.* 2005). For other polymers,
31
32 they can be approximated using an empirical structure / diffusion coefficient
33
34 relationships such as the Piringier equation (Begley *et al.* 2005), which
35
36 overestimates the actual values (worst case). In the general case, the use of an
37
38 “intrinsic” diffusion coefficient (measured by the Moisan or by the three-layer
39
40 test) is a good predictive tool with an acceptable approximation.
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44 ***What about assuming $KF/P=Infinite$?***

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46 Simulations of migration kinetics for different K values (Figure 10) indicate that
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48 partition effects influence mainly the second part of the kinetics, *after the lag*
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4 *time*. Even if the entire kinetics (a) are different, the initial parts (b) are very
5 similar. No significant differences are observed during the lag time period [see
6 also first time derivatives (c) and (d) respectively] in the initial stages of the mass
7 transfer into the liquid (before maximum flux / see time derivative kinetics). The
8 second part is of little interest if we focus on a rough idea of the lag time, for
9 instance to compare a lag time with a shelf life when the functional barrier
10 efficiency has to be evaluated. If one is interested only by the lag time period,
11 using MULTIWISE with the assumption $K = \text{infinite}$ (or in practice any arbitrary
12 value) leads to a correct estimation of the lifetime. STORAGE, the simplified
13 software, does not take into account K values.
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26 ***What about assuming $H/p \rightarrow \text{Infinite}$?***

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28 Three different situations of the mass transfer coefficient H/P are possible:

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30 $H/P = 0$: no migration. This value of the parameter can be used in
31 Multiwise to describe diffusion during storage of empty containers before
32 packaging foods for non volatile contaminants.
33
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36 $H/P = 1$ ($H/P \rightarrow \text{infinite}$): this is the (worst) case generally used; the
37 partition equilibrium on the surface is instantaneously reached.
38

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40 $H/P > 0$ but low (in the $10^{-11} - 10^{-8}$ range): in this case, the migration of
41 the contaminant is partly controlled by its rate of evacuation from interface to
42 food.
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46 Since the prediction of H/P values has never been studied in literature, it is
47 unfortunately not possible to propose a better approach. Assuming $H \rightarrow \text{infinite}$ is
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4 an overestimation, contributing to a worst case approach, but very far from the
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6 behaviour of real viscous foodstuffs.
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10 ***What about the partition coefficient at barrier / polymer interface: diffusion***
11 ***and solubility barriers?***
12

13
14 The influence on migration of the partition coefficient of the migrant between
15 polymer layers is illustrated on Figure 11. This is obtained by a simulation using
16 MULTIWISE, for a three-layer material, with the contaminant initially located in
17 layer 2, diffusing through the barrier (layer 1) before migrating into food. If the
18 substance has a polarity very different from that of the barrier, its partition
19 coefficient between layers 1 and 2 may change dramatically. In all simulations,
20 the diffusion coefficients in all layers are the same: $D = 4.4 \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, which
21 corresponds to trichloroethane in polypropylene, calculated from the Piringer
22 equation (Begley *et al.* 2005). It is seen that this partition coefficient strongly
23 influences the migration kinetics, but has no influence on the lag time.
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33 This is the case of polar substances, coming from instance from a polar substrate
34 like paper (here layer 3). If the barrier is apolar (like polypropylene), the
35 migration of the polar substance will be kept to a very low level even after the lag
36 time.
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43 This illustrates that numerous possibilities exist to design a functional barrier, by
44 playing on the diffusion behaviour, but also on the partition behaviour between
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4 different layers. With $K_{\text{barrier/layer 2}} = 0.01$, the barrier is a very efficient
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6 solubility barrier.
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14 CONCLUSION

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18 In principle, a large set of parameters is needed to assess the efficacy of a
19 functional barrier: diffusion coefficients, activation energy, mass transfer
20 coefficients at the different interfaces and partition coefficients, plasticization
21 parameters.
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28 It is possible to simulate the behaviour of functional barriers, using some
29 assumptions for the parameters.
30

31 Parameters which are overestimated:

- 32 - the diffusion coefficients at melted state (Pennarun *et al.* 2004a) and at 40°C
33 (Feigenbaum *et al.* 2005, Dole *et al.* 2006).
34
- 35 - KF/P : for a worst case, and for comparing predicted migration to a legal limit, K
36 has to be overestimated, and $KF/P = \text{infinite}$ can be used. Nevertheless, if the
37 criteria for evaluation of the functional barrier is the lag time, KF/P has no
38 influence and any value can be taken.
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- 40 - Hl/p : can be assumed infinite. But as it is a critical value, it could be determined
41 with model migration experiments from very thin films (few μm).
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6 Parameters which have to be determined: h_c

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8 PROCESS proposes default values. As it plays a major role, h_c should be
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10 experimentally determined from surface temperature kinetics (Pennarun *et al.*
11
12 2004a).

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16 Parameters for which there is no value currently available:

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18 The activation energy of diffusion in melted state, E_a , is also a key parameter.
19
20 The lower E_a , the larger is the barrier pollution. DMA in different polymers
21
22 display very large differences. In PROCESS, these values are used. But the
23
24 structure of the migrant probably plays an important role, which has not been
25
26 studied up to now. Pending more data, we propose to use an average value $E_a = 50$
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28 kJ mol^{-1} .

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32 The partition coefficients between polymer layers have a very important effect on
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34 migration kinetics, but only a reduced effect on the lag time. In the FAIR project,
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36 we focused on functional barriers linked to restricted diffusion properties. With
37
38 such diffusion barriers, the larger the molecular weight of the migrant, the lower
39
40 its diffusion coefficient (at least in first approximation) and the larger the barrier
41
42 effect. This work also illustrates how functional barriers may work based on
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44 opposite polarities and poor solubility of the migrant in the barrier. Solubility
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46 barriers act in a complementary mechanism, reducing the migration of substances
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4 with extreme polarities. Obviously the latter mechanism is less general, but it may
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6 be useful especially when the identity of the migrant is known.
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10 The examples described illustrate both the multiple effects influencing migration
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12 and how the software given allow to optimise a material in function of all these
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14 parameters. PROCESS and STORAGE, using default values of parameters allow
15
16 a quick classification of materials on the basis of the lag phase. If more data are
17
18 available, MULTITEMP and MULTIWISE can describe the expected migration
19
20 kinetics.
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23 In many cases, however, more realistic data are needed. Using only
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25 overestimations of migration or of lag phase may lead to the conclusion that no
26
27 functional barrier exist, which may be too severe. There is then the need of more
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29 accurate determinations of some parameters.
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32 33 34 35 **ACKNOWLEDGEMENT** 36

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39 The work reported here was achieved in the frame of the FAIR CT984318 EU-
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41 funded research programme. The European Commission DG Research, the
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43 Region Champagne Ardenne and Institut National de la Recherche Agronomique
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45 are acknowledged for financial support of this work.
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CAPTIONS

Table 1: diffusion coefficients of surrogates, obtained by the Moisan method and by migration experiments from (HDPE/HDPE-surrogates/HDPE) sandwiches (300 μm)

Figure 1: Principle of the migration test: a three-layer (Virgin/Contaminated/Virgin films) is in contact with the simulant on one side, in a stainless steel cell

Figure 2: Experimental 2,4-Dimethoxyacetophenone distribution in a multilayer [EVOH/EVOH-DMA/EVOH] after processing at 210°C. Possible fits are on figure 3.

Figure 3: DMA diffusion profile corresponding to an evaporation of the diffusant at the surface with $HP/a = 0.001 \text{ m s}^{-1}$

Figure 4: DMA diffusion profiles, assuming no evaporation at the surface ($HP/a = 0 \text{ m s}^{-1}$)

Figure 5: Classification of functional barrier efficacy: thickness needed to get the concentration on the surface in contact with food at 5% of the initial concentration

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4 in the recycled layer, based on very worst case D (diffusion coefficient of DMA;
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6 Pennarun *et al.* 2004a). Simulated with PROCESS for $h_c = 255 \text{ W m}^{-2} \text{ s}^{-1}$, process
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8 time 0.1 s. Functional barrier thickness is 1/3 of the whole material thickness.
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10 Each label mentions polymer type and processing temperature.
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14 Figure 6: Migration kinetics at 40°C of trichloroethane from [Virgin
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16 PP/contaminated PP/Virgin PP (300 µm)] into olive oil and ethanol
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20 Figure 7: Migration kinetics at 40°C of trichloroethane from [Virgin
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22 PP/contaminated PP/Virgin PP (300 µm)] three-layers into water. The vertical
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24 line indicates the lag time with olive oil and with ethanol
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28 Figure 8: influence on migration kinetics and on lag time of the food/polymer
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30 mass transfer coefficient. Calculation made with MULTIWISE, assuming a three
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32 layer material (25-50-25 µm), the migrant is initially in layer 3 ($C_{1,t=0} = 0$, $C_{2,t=0} =$
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34 0 , $C_{3,t=0} = 500 \text{ mg/kg}$), with $K_{pol1/pol2} = K_{pol2/pol3} = 1$, $K_{F/P} (K_{liquid/pol1}) =$
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36 1 ; $D_{pol1} = D_{pol2} = D_{pol3} = 4.4 \cdot 10^{-11} \text{ cm}^2 \text{ s}^{-1}$.
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42 [Virgin PP/contaminated PP/Virgin PP (300 µm)] three-layers into water.
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4 Figure 10: simulation of migration kinetics, using different food/packaging
5 partition coefficients a, b: $F_c = \text{migration (kg m}^{-2}\text{)}$; c, d: derivative of migration
6 $(\text{kg m}^{-2} \text{ s}^{-1})$ b and d are enlargements of a and c respectively
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11 Figure 11: simulation of the influence on migration of the partition coefficient between
12 polymer layers in a system:
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14 FOOD / POLYMER 1 (250 μm) / POLYMER 2 (500 μm) / POLYMER 3 (250 μm)

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16 (K12) is the partition coefficient between polymer layers 1 and 2, $K_{23} = K_{F/1} =$

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18 1, all other parameters being identical. Calculation with MULTIWISE, assuming

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20 all the migrant initially in layer 2 ($C_{1,t=0} = 0$, $C_{2,t=0} = 500$, $C_{3,t=0} = 0$ ppm). The

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22 diffusion coefficient is $4.3 \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ in all polymer layers.
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Simulant →	Diffusion coefficient D ($10^{-10} \text{ cm}^2 \text{ s}^{-1}$)		
	Moisan test ("intrinsic" D)	Migration experiment with three- layer material (apparent D)	
↓ Surrogate	None	Ethanol	Olive oil
Toluene	24	18	15
Chlorobenzene	26	20	14
1,1,1- Trichloroethane	6.5	3.8	2.9
Phenylcyclohexane	2.7	1.9	1.6
Benzophenone	1.8	3.8	3.2
Methyl margarinate	1.7	1.7	0.8

Table 1: diffusion coefficients of surrogates, obtained by the Moisan method and by migration experiments from (HDPE/HDPE-surrogates/HDPE) sandwiches (300 μm)

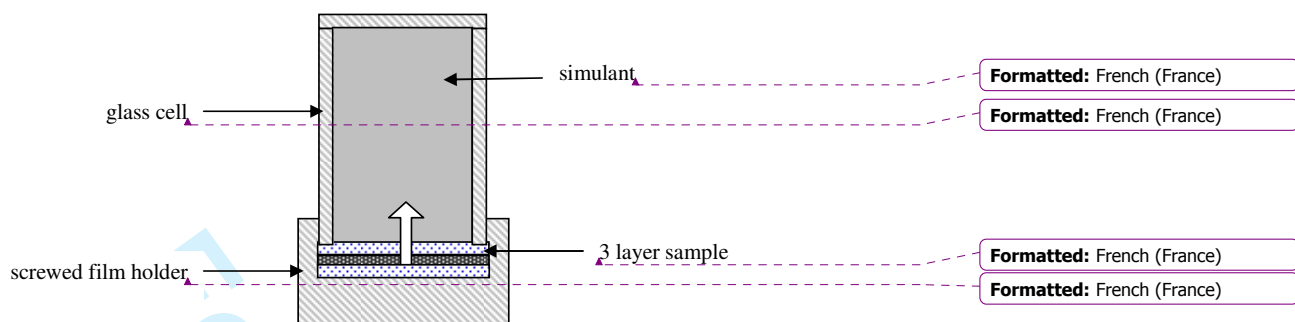


Figure 1: Principle of the migration test: a V/C/V three-layer

(Virgin/Contaminated/Virgin) is in contact with the simulant on one side, in a

stainless steel cell

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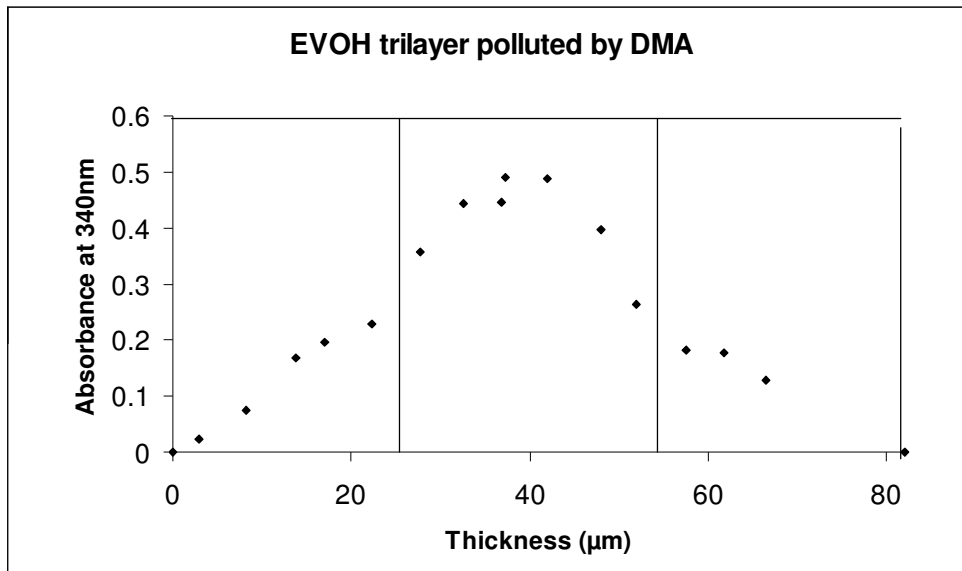


Figure 2: Experimental 2,4-Dimethoxyacetophenone distribution in a multilayer [EVOH/EVOH-DMA/EVOH] after processing at 210°C. Possible fits are on figure 3.

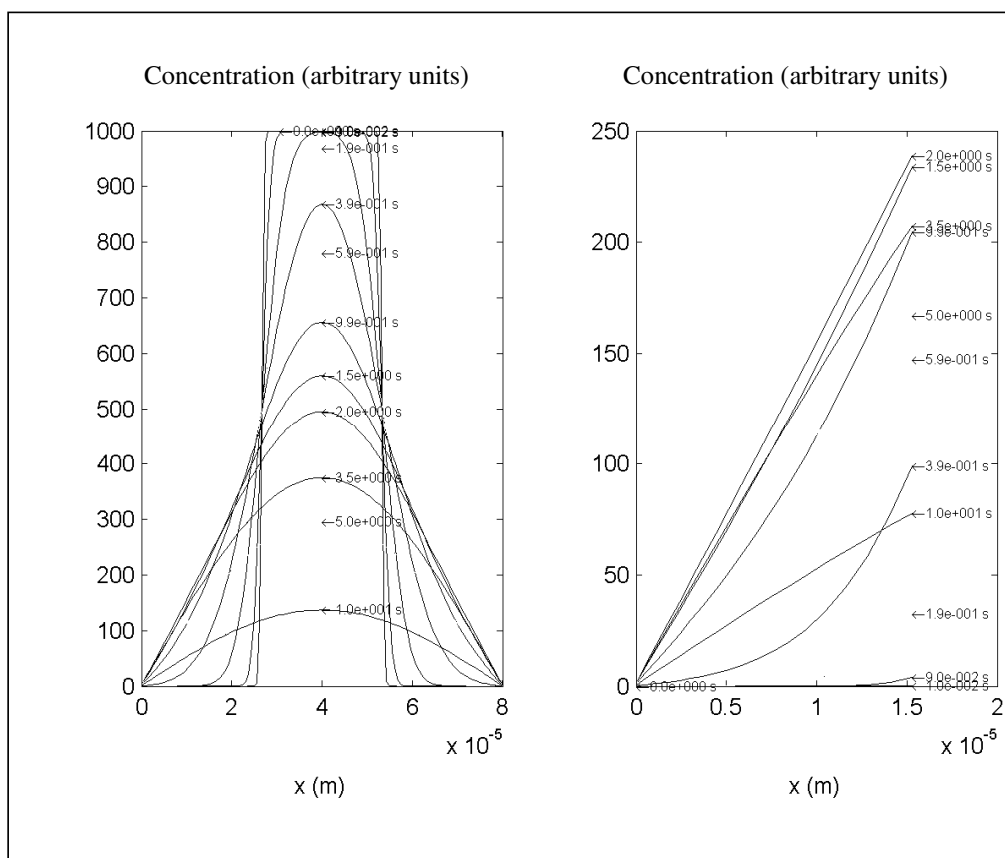


Figure 3: 2,5-dimethoxyacetophenone diffusion profiles (corresponding to an evaporation of the diffusant at the surface with $HP/a = 0.001 \text{ m s}^{-1}$

Concentration (arbitrary units)

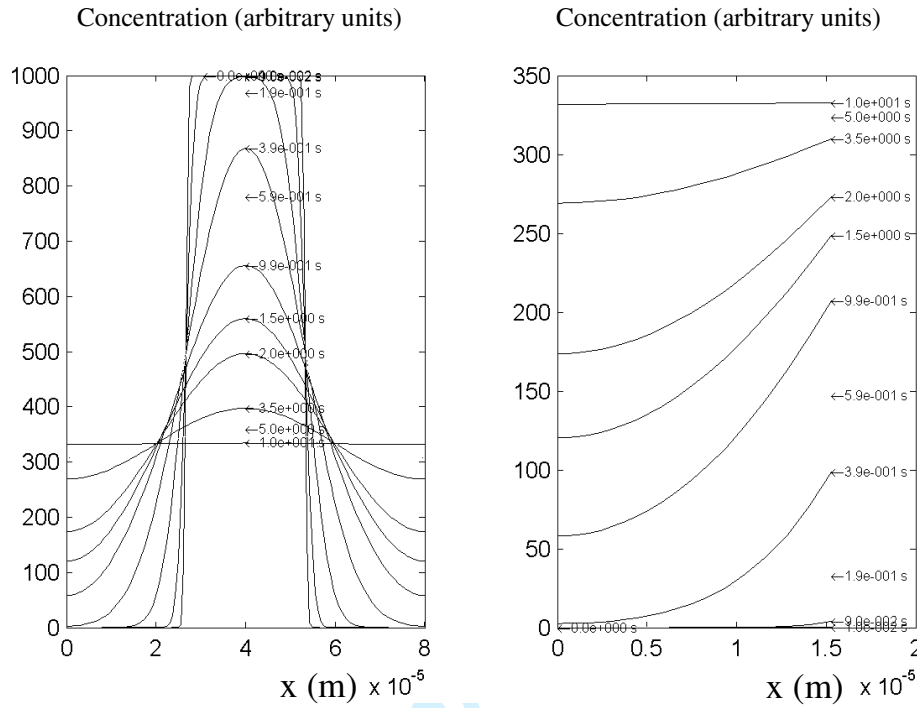


Figure 4: DMA diffusion profiles, assuming no evaporation at the surface ($HP/a = 0 \text{ m s}^{-1}$). Figure on the right is an expansion of the interface region.

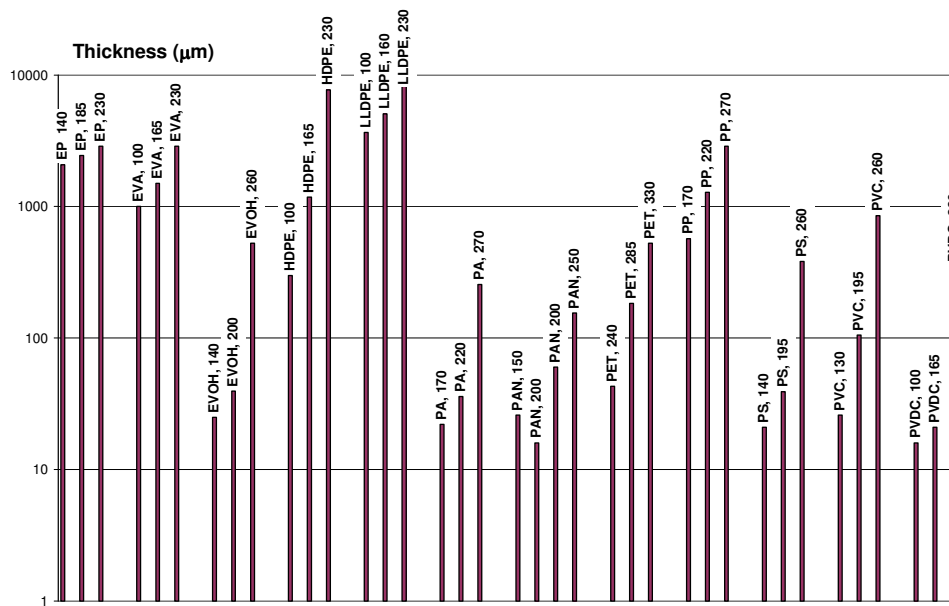


Figure 5: Classification of functional barrier efficacy: thickness needed to get the concentration on the surface in contact with food at 5% of the initial concentration in the recycled layer, based on very worst case D (diffusion coefficient of DMA; Pennarun *et al.* 2004a). Simulated with PROCESS for $hc = 255 \text{ W m}^{-2} \text{ s}^{-1}$, process time 0.1 s. Functional barrier thickness is 1/3 of the whole material thickness. Each label mentions polymer type and processing temperature.

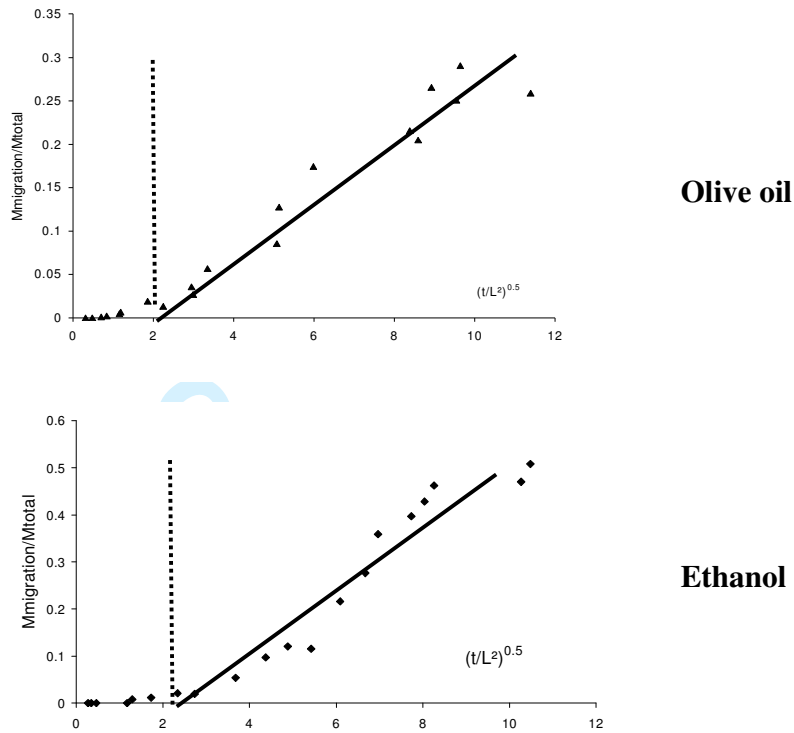


Figure 6: Migration kinetics at 40°C of trichloroethane from [Virgin PP/contaminated PP/Virgin PP (300 μm)] into olive oil and ethanol [t in h, L (μm) is the functional barrier layer thickness]

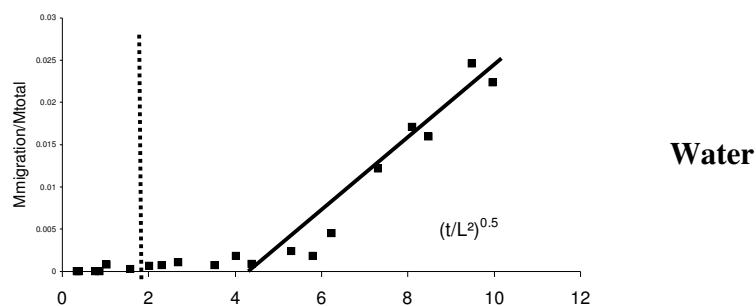


Figure 7: Migration kinetics at 40°C of trichloroethane from [Virgin PP/contaminated PP/Virgin PP (300 μm)] three-layers into water. The vertical line indicates the lag time with olive oil and with ethanol [t in h, L (μm) is the functional barrier layer thickness].

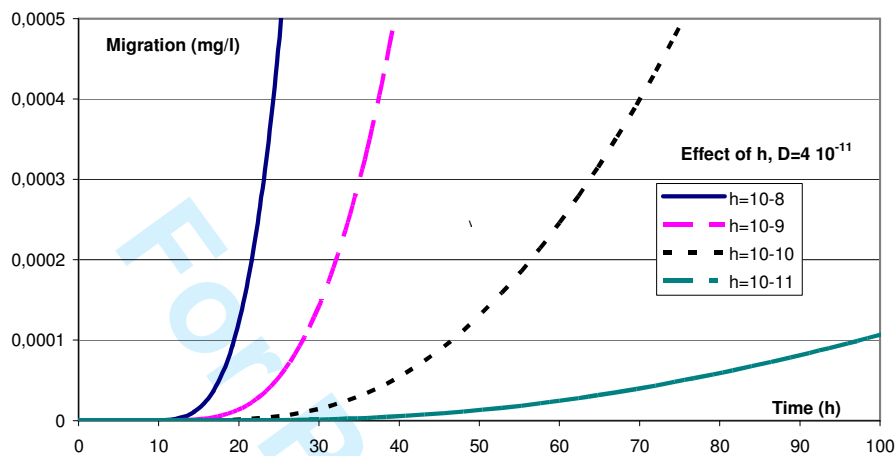


Figure 8: influence on migration kinetics and on lag time of the food/polymer mass transfer coefficient. Calculation made with MULTIWISE, assuming a three layer material (25-50-25 μm), the migrant is initially in layer 3 ($C_{1,t=0} = 0$, $C_{2,t=0} = 0$, $C_{3,t=0} = 500$ ppm), with $K_{\text{pol1/pol2}} = K_{\text{pol2/pol3}} = 1$, $K_{\text{F/P}} (K_{\text{I/pol1}}) = 1$; $D_{\text{pol1}} = D_{\text{pol2}} = D_{\text{pol3}} = 4.4 \cdot 10^{-11} \text{ cm}^2 \text{ s}^{-1}$.

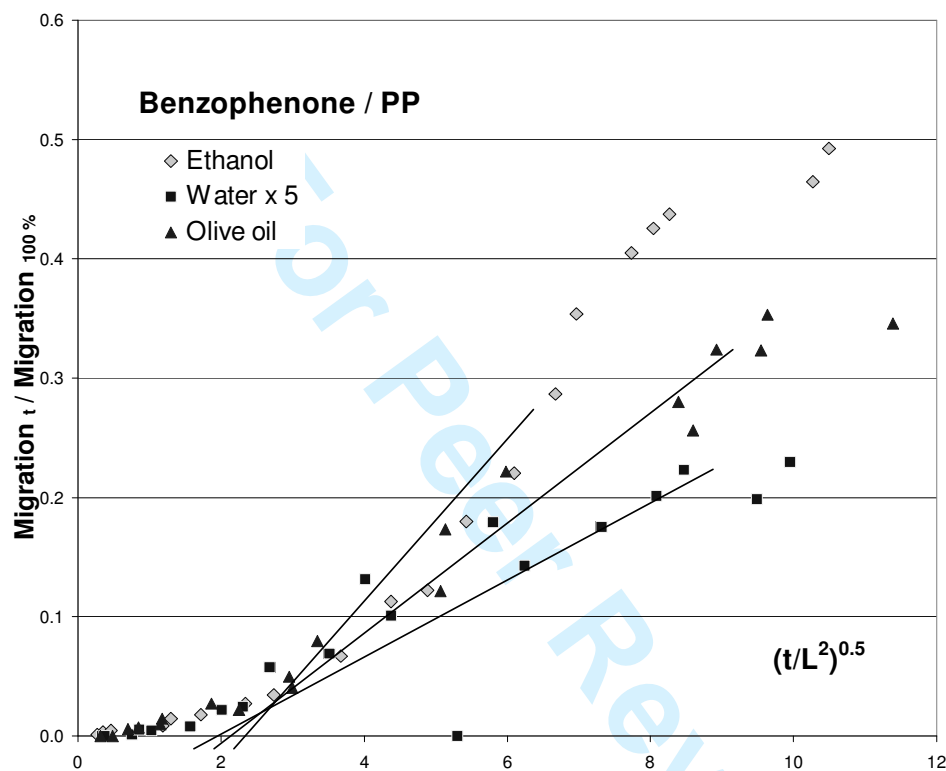


Figure 9: Migration kinetics at 40 °C of Benzophenone from [Virgin PP/contaminated PP/Virgin PP (300 μm)] three-layers into water [t in h, L (μm) is the functional barrier layer thickness].

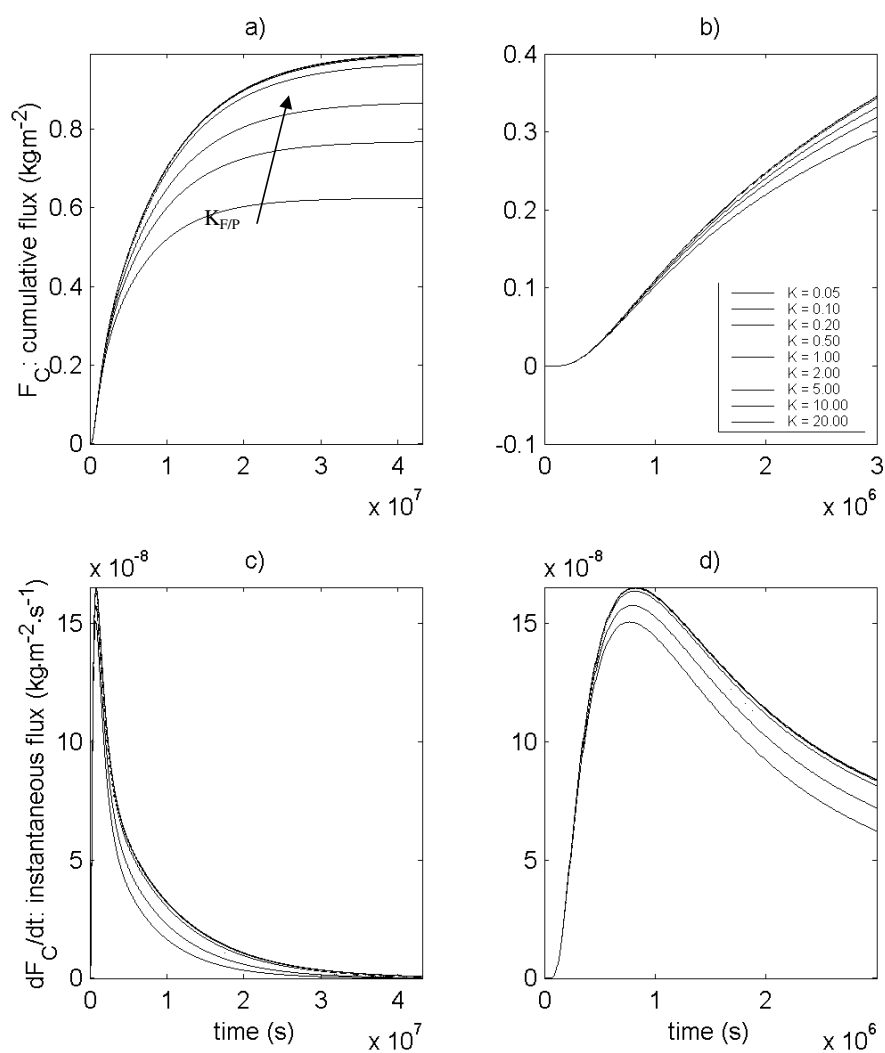


Figure 10: simulation of migration kinetics, using different food/packaging partition coefficients: a, b: F_C = migration (kg m^{-2}); c, d: derivative of migration ($\text{kg m}^{-2} \text{s}^{-1}$)

b and d are enlargements of a and c respectively

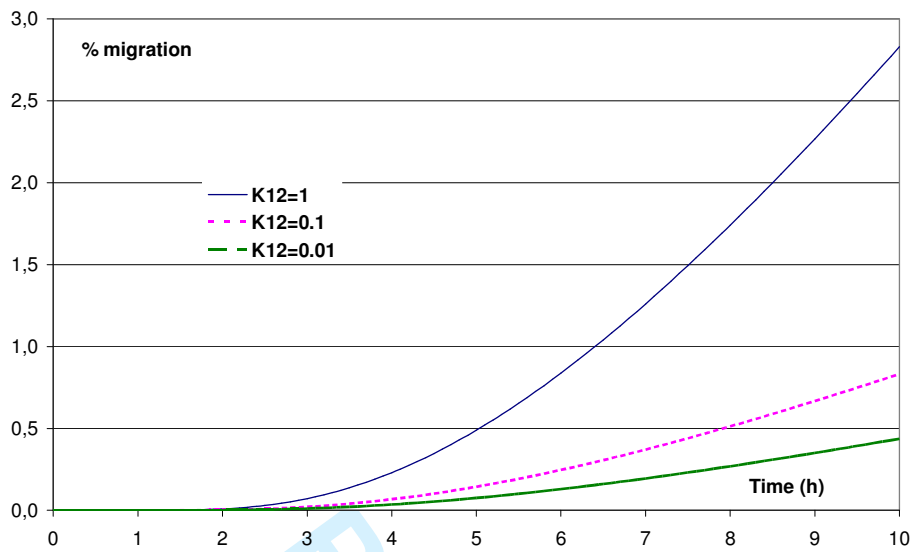


Figure 11: simulation of the influence on migration of the partition coefficient between polymer layers in a system:

FOOD / POLYMER 1 (250 μm) / POLYMER 2 (500 μm) / POLYMER 3 (250 μm)

(K12) is the partition coefficient between polymer layers 1 and 2, $K_{23} = K_{F/1} = 1$, all other parameters being identical. Calculation with MULTIWISE, assuming all the migrant initially in layer 2 ($C_{1,t=0} = 0$, $C_{2,t=0} = 500$, $C_{3,t=0} = 0$ ppm). The diffusion coefficient is $4.3 \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ in all polymer layers.