

Functional barriers: from complex modelling to simplified evaluation

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Functional barriers: from complex modelling to simplified evaluation

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KEYWORDS

Food packaging, migration, recycling, functional barrier, modelling, safety
assessment

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ABSTRACT

Functional barriers are parts of multilayer packaging materials, deemed to protect the food from migration of a broad range of contaminants e.g. associated to reused packages. 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 to model diffusion in multi-layer films. MULTITEMP describes diffusion during processing (high temperature during a short time, followed by cooling). The concentration profiles thus calculated are taken over by a second software, MULTIWISE, which simulates diffusion in successive isothermal steps like hot filling and storage. Software PROCESS and STORAGE can be used as assistance to design of materials. Experimentally diffusion and migration of trichloroethane, toluene and benzophenone were monitored from [Polyolefin/contaminated Polyolefin] multilayer structures. The diffusion coefficient and the lag time did not depend on the simulant with lipophilic simulants. Migration of lipophilic migrants into water exhibited longer lag times, an effect which was attributed to the mass transfer coefficient at interface. The influence of all the parameters needed for the calculations, for a good description of the experiments and for prediction is discussed.

INTRODUCTION

Functional barriers are used in packaging to protect food from the migration of accidental pollutants 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 implies to (i) determine if no pollution of the barrier occurs during processing of the multilayer material (Pennarun et al 2004a, Franz et al 1997, Perou et al 1997) and to (ii) determine if 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)

Considering that 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 Piringier data bases and equations involving a large molecular weight range (Baner *et al* 1996, Begley *et al* 2005)

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But migration is obviously not controlled only by diffusion. The practical use of simulation tools implies to introduce default values for partition coefficients, heat transfer, heat diffusion, mass transfer, diffusion coefficient activation (Dole *et al.* 2006), factors describing the effect of plasticization on diffusion (Reynier *et al.* 2002).

This paper proposes the use of both complex and simplified modelling tools and discusses the consequences of generally necessary approximations and default values. The discussion is focused on properties of accidental pollutants of interest, which are supposed to be rather low molecular weight compounds (Feigenbaum *et al.* 2005). In order to simplify the discussion, pollution at molten state and migration will be studied from different experiments. Particularly, migration from functional barriers is studied from multilayer materials obtained from a specific processing method minimizing pollution at molten state.

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MATERIALS and METHODS

Materials

** Measurement of diffusion coefficients of DMA during processing using UV microspectrophotometry*

An EVOH trilayer film was processed with an industrial extruder (CRYOVAC, US) at 210°C. The inner layer was polluted by 2,5-dimethoxyacetophenone

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6 (DMA). After co-extrusion the sample was stored below 0°C to prevent further
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8 diffusion. 30 µm microtomic cross sections were then analyzed with a UV
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10 microspectrophotometer (Carl Zeiss UV-visible spectrophotometer equipped with
11
12 a Xenon lamp and a microscope unit for analysis of small areas). The analysed
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14 area is a circle with radius 1 µm. The concentration gradient of DMA is recorded
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16 from the maximum absorption peak of DMA at 330 nm (Pennarun *et al.* 2004a).
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22 **** Measurement of diffusion coefficients at 40°C***
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24 The experiments are based on the measurement of a concentration gradient in a
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26 stack of PP virgin films after a given time of contact with a source spiked with
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28 surrogates. A homogeneous solid source is obtained by melting a polyethylene
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30 wax together with the surrogates (representing the contaminants) in an appropriate
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32 mould. Usual concentrations of surrogates in the source are about 1000 ppm. The
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34 stack of PP films is obtained under the action of both temperature and pressure. It
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36 is essential to check visually that there is an intimate contact between the different
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38 films of the stack and that no air bubbles remain, as this could introduce important
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40 errors. Source and stack are assembled under slight pressure to get a good contact
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42 between them, and are stored at a controlled temperature (40°C in this project) in
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44 an oven. During the contact, surrogates diffuse from the source into the stack,
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46 through the films. After a given time, each film of the stack is separated and
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48 extracted separately with dichloromethane, at 40°C for 1 day. Finally surrogates
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50 are determined quantitatively by gas chromatography (GC).
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Migration testing

The migration tests are made with a three-layer film in contact with a simulant.

Several three-layer films (virgin/contaminated/virgin layers, noted V/C/V) are prepared by co-extrusion. A Scamex (Crosnes, France) microextruder was equipped with a short slit die in order to minimize contact time between layers at molten state. A calander was placed at 1 cm after the co-extrusion die, which also contributed to minimize the cooling time. Samples were rapidly cooled at -30°C just after extrusion to prevent further diffusion. Migration tests were started few hours after this processing operation. Samples with homogeneous thickness selected, and then immersed into a migration cell filled with the simulant (water, ethanol, or olive oil). The cells are stored at a controlled temperature and the surrogates diffuse through the virgin polymer layer into the simulant (Figure 1). The concentration of migrating surrogates is determined at different times by analysing the simulant. In order to take into account potential variations of initial concentrations in the film, it is important to analyse also the three-layer film at the end of the migration test: the initial concentration is equal to [migrated quantity + quantity remaining in film, determined by extraction at the end of the test].

Kinetics displayed are expressed in function of $(t/L^2)^{0.5}$ in order to take into account local variations of the thickness from sample to sample. The thickness of each sample was measured by visible microscopy.

Modelling mass transport phenomena

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

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

Beta versions of the different software developed for the project can be downloaded as a freeware at: [http://www.inra.fr/Internet/Produits/securite-
emballage/pagefr.html](http://www.inra.fr/Internet/Produits/securite-emballage/pagefr.html)

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.

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8 * *Estimation of the parameters*: diffusion parameters and their thermal activation
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10 can be approximated using reference data of a fast diffusing (worst case) probe
11 (surrogate) (see discussion below). The first problem is that it is difficult to
12 appreciate the importance of matter losses both in extruder and during cooling of
13 co-extruded film. These phenomena are linked to the volatility of the species but
14 also to the geometry of the machines. The “worst case approach” (in terms of
15 migration prediction), consists in considering that no losses occur. The second
16 problem is to calculate the temperature gradient (across the thickness and as a
17 function of time). This response strongly depends on the heat convection
18 parameters (i.e. in fact on the conditions of cooling) and not much on heat
19 diffusion, which can be approximated easily by default parameters for all
20 polymers at molten state.
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39 **Simplified tool: PROCESS software**

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41 A reduced number of parameters seems relevant for a rough description of
42 diffusion during the process in worst case situations. This leads to simplified
43 software, called PROCESS, taking into account a reduced number of variables,
44 and describing qualitatively the influence of the range of their variation.
45 PROCESS considers the type of polymer (described as the diffusion coefficient of
46 DMA at the melt temperature), the packaging thickness range (both absolute
47 value of thickness L – from 10 μm to 20 mm - of material and relative thickness
48 of the functional barrier fb – arbitrarily taken as 33 % in the first version of the
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software), the extrusion time (see below), the extrusion temperature and the heat transfer coefficient h_c (from 10 to 200 $\text{W m}^{-2} \text{s}^{-1}$, considered here as a flux). PROCESS considers a residence time in a mould or in a co-extrusion dye at a constant temperature, followed by a convective cooling down to room temperature, with an overall duration of both stages of 60 s. PROCESS calculates abacuses of percentages of concentration of DMA (the model pollutant) of the functional barrier (average concentration) and of the external surface (local concentration).

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

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6 differences based on Klopfenstein-Shampine family of numerical differentiation
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8 formulas for time marching.
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10 11 12 **Migration of pollutants into food: MULTIWISE software**

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17 The diffusion is described by the second Fick's law. The diffusion coefficient is a
18 function of the local concentration of food constituents (or of the food simulant)
19 in the plastic at time t. One diffusion coefficient of a given surrogate is defined for
20 each layer in absence of food constituent; its value is allowed to vary with the
21 local concentration of the swelling simulant. An exponential relation between D
22 and food constituent (simulant) concentration is assumed.
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32 $D \text{ at } t = \text{initial } D [\text{entered value}] \times \exp(B \times \text{simulant concentration at } t)$

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34 The parameter B characterises the swelling effect of the food constituent
35 (simulant). When B=0, the diffusion coefficient does not depend on the simulant
36 concentration – no “swelling” nor “plasticizing” effect.
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41 42 * Influence of Food sorption

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44 Food sorption is described by the second Fick's law. The diffusion coefficient of
45 food constituents into the polymer is a function of the local food concentration at
46 time t. An exponential relationship between D_{food} and food concentration is
47 assumed.
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55 56 * Mass transfer of pollutant at interfaces:

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HP/a and HI/P are the mass transfer coefficients at the polymer /air and at the liquid (food) / polymer interfaces. Three different situations are generally possible for H (HP/a and HI/P) parameters:

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

H is “infinite”: the transfer from the interface is instantaneous. As the external volume is considered infinite, the concentration on the surface is equal to zero.

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

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

Simplified tool: Storage software:

STORAGE simulates the migration of different pollutants from recycled plastic films (in symmetrical materials containing a functional barrier) into food during contact with food.

As for PROCESS, STORAGE is based on a database of simulated results. New results are either linearly or non linearly (cubic Hermite interpolation) interpolated through a suitable grid of reference conditions.

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 days)

Output: level of migration into food.

Assumptions: A diffusive mass transport is assumed, with a worst case scenario: no external resistance between film and food. A one side contact is assumed.

Note: in the software available on the web site, for simplification, the h_c (MULTITEMP), H_l/p (MULTIWISE) parameter are just named H . H_p/a is not taken into account. H_l/p can be adjusted.

RESULTS AND DISCUSSIONS

DIFFUSION DURING PROCESSING OF FUNCTIONAL BARRIERS

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

Two essential observations can be made: (i) the virgin layer is polluted and (ii) the diffusion has reached the external surface. The slope of the profile near the surface suggests an external rate limiting desorption by evaporation.

This profile shape can be simulated by numerical calculation assuming that the diffusion behaviour of EVOH [$D=f(T)$] is a simplified two-step process:

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

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

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

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

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However, the possibility to fit these specific data as in Figure 3 should not be considered as a validation of a model, since the concentration 0 at the polymer / air interface as well as the profile shape suggest that an important evaporation has taken place. Modelling of evaporation would involve too many parameters, most of them being difficult to evaluate, such as the average (in the considered temperature range) rate of evaporation at the surface, the temperature profiles...

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This is why the overestimation method should in first instance be used as an indicative tool to decide whether a pollution of the barrier layer is likely or not to occur during processing. This should be sufficient to describe most practical situations, which are expected to be close to either of the two extreme situations:

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- When there is no significant pollution of the barrier during processing, the migration step can be calculated independently assuming no pollution at all

(vertical profiles). With PET, it has been shown experimentally that the pollution of a functional barrier of a bottle is negligible during processing (Pennarun *et al.* 2004a).

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

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

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

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

- if the barrier is not efficient, no further calculations are necessary.

Selection of functional barrier materials on the basis of behaviour during processing

The simplified description used in PROCESS allows classifying the polymers in function of their diffusion behaviour at their melt temperature.

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The thickness needed to maintain $C_{fb} \leq 0.05 C_0$, at different processing temperatures was calculated for all the polymers in the data base of PROCESS. These times should not be considered as absolute values, as they are calculated in extremely worst case: the diffusion coefficients used are those of DMA. $h_c = 255 \text{ W m}^{-2} \text{ s}^{-1}$, relative functional barrier thickness is 1/3 of the whole material, and the process time $t_e = 0.3 \text{ s}$. On Figure 5, each label mentions polymer type and processing temperature. Based on the behaviour of DMA, polymers which are glassy at room temperature are by far the best diffusion barriers.

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

Figure 5 allows interpretations like: “a 50 μm PVDC functional barrier is equivalent to 10 000 μm LLDPE”.

The classification thus obtained corresponds roughly to the efficiency of gas barrier polymers: the higher is the glass temperature, the better is the barrier. Again, since this scale is based on the behaviour of DMA, it may take into account specific interactions of this surrogate with the polymer.

Which parameters can be used for prediction of diffusion during processing?

For prediction purpose, four parameters are essential: D , h_c , E_a and HP/a . Let us examine these parameters one by one.

What about D and E_a during processing?

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In the software, the diffusion coefficient and the activation energy used are those of DMA, the reference compound. This is probably a worst case, as DMA has a low molecular weight: low molecular weight substances have high diffusion coefficients and low activation energies (Dole *et al.* 2006). In case of recycling, where the identity of the possible pollutant is unknown, one should take into account such worst case, lower molecular weight reference compounds. This should not lead to major differences as the dependence of D with molecular weight is expected to be low at high temperature (Dole *et al.* 2006). However it would be interesting to have D and Ea data available for several reference compounds, with different chemical groups, in order to better take into account possible specific [diffusant – polymer] interactions. The activation energies measured for DMA in melted polymers were up to 110 kJ/mole in polyacrylonitrile (Pennarun *et al.* 2004a). Since the worst case corresponds to the lowest value (slightest decrease of D during cooling), more information should be obtained in this field. When using the MULTITEMP software to describe the diffusion of an unknown contaminant, a default value of 50 kJ/mole is recommended for diffusion in melted state.

What about hc?

The larger is hc, the quicker is the cooling and the steeper is the decrease of D once the layers are assembled. In the case of PET co-injection, different scenarios, corresponding to basically different cooling conditions, were envisaged. Typical values:

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

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

$hc = 10 \text{ W m}^{-2} \text{ s}^{-1}$: cooling by natural convection of air

The worst case situation in all cases would be $hc = 0 \text{ W m}^{-2} \text{ s}^{-1}$. But this has no meaning, as the polymer would not be allowed to cool.

hc values have therefore to be measured in a process, which can be achieved with an infrared camera, by following surface – temperature kinetics.

What about H_p/a ?

If evaporation takes place during processing (large H_p/a), the average and the surface concentration of the pollutant (and consequently its migration) will be lower (see figure 2), which contributes to the consumer's safety. The current version of MULTITEMP however describes processing in a mold, which is a worst case situation ($H_p/a = 0$, no evaporation). The future version will include this variable. H_p/a values can be determined according to Vergnaud (1991).

MIGRATION THROUGH FUNCTIONAL BARRIERS

The aim of this part of the work is to establish whether the simplified model MULTIWISE, with a simple set of default parameters, assuming complete migration at equilibrium and no rate limiting mass transfers, can describe the initial part of migration kinetics. The early stages of migration are the most

critical in terms of risk assessment of the capacity of a functional barrier to protect a food.

The first step was to measure intrinsic diffusion coefficients of the surrogates in the polymer, i.e. values which could be considered as true values, not apparent values. This required tests conducted in absence of liquid simulants, which often plasticize the polymers. The Moisan test is well adapted to this requirement (table 1).

The second step was to apply the simplified model to fit experimental migration kinetics from three-layer materials (prepared with the polluted layer as middle layer) into olive oil and ethanol. The experiments were run for a complete set of surrogates in PP and in HDPE. Kinetics are shown for HDPE in Figure 6. The experiments were carefully designed, as follows: (i) PP and HDPE, which are poor barriers, were used in order to have quick results (ii) the total thickness (about 300 μm) was adjusted to have a lag time of several hours. Use of a micro-extruder allowed minimising the diffusion in the molten state, due to a very short contact time at high temperature; moreover a calander was placed at 1 cm after the co-extrusion die, which also contributed to minimize diffusion during the cooling time. It could thus be assumed that no diffusion occurred during the processing step. In order to have also no diffusion between date of processing and date of start of migration tests, the samples were stored at -30 °C immediately after their processing.

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Intrinsic (in HDPE films) and apparent (into simulants) diffusion coefficients were determined from Moisan tests and for migration (from HDPE three-layers into ethanol and olive oil) experiments respectively (Table 1). Fits of experimental results were made with MULTIWISE, assuming very large values of $Hl/P = 1$ (equivalent to Hl/P tends to ∞). These D values all lie in the same order of magnitude, which suggests that the approach should be further simplified, and that swelling effects by the food could be neglected.

On the other hand, it may seem surprising at first glance that apparent diffusion coefficients with olive oil are not higher than intrinsic ones, and that plasticization of the functional barrier does not play a role. This apparent contradiction can be solved by considering general knowledge on plasticization: all surrogates in this experiment are low molecular weight species (the low molecular weight was one of the criteria for the selection of surrogates), which are less influenced by plasticization than higher molecular weight compounds, like normal additives (Reynier *et al.* 2002).

Results for (PP/polluted PP/PP, not displayed here) three-layer materials (intrinsic D without solvent, and apparent D with ethanol and with olive oil) show a similar situation: the lag times obtained for the migration of the low molecular surrogates into both simulants are very close and they can be predicted from “intrinsic” diffusion coefficients.

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

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

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8 **Prediction of migration kinetics: which values are to be used for the**
9 **calculations?**
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15 ***What about D in storage conditions?***
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17 Diffusion coefficients at ambient temperature can be approximated using
18 reference data obtained with fast diffusing, low molecular weight probes tabulated
19 for 14 polymers (Dole *et al.* 2006, Feigenbaum *et al.* 2005). For other polymers,
20 they can be approximated using an empirical structure / diffusion coefficient
21 relationships such as the Piringier equation (Begley *et al.* 2005), which
22 overestimates the actual values (worst case). In the general case, the use of an
23 “intrinsic” diffusion coefficient (measured by the Moisan or by the three-layer
24 test) is a good predictive tool with an acceptable approximation.
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39 ***What about assuming $Kl/P=Infinite$?***
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41 Simulations of migration kinetics for different K values (Figure 10) indicate that
42 partition effects influence mainly the second part of the kinetics, ***after the lag***
43 ***time***. Even if the entire kinetics (a) are different, the initial parts (b) are very
44 similar. No significant differences are observed during the lag time period [see
45 also first time derivatives (c) and (d) respectively] in the initial stages of the mass
46 transfer into the liquid (before maximum flux / see time derivative kinetics). The
47 second part is of little interest if we focus on a rough idea of the lag time, for
48 instance to compare a lag time with a shelf life when the functional barrier
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6 efficiency has to be evaluated. If one is interested only by the lag time period,
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8 using MULTIWISE with the assumption $K = \text{infinite}$ (or in practice any arbitrary
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10 value) leads to a correct estimation of the lifetime. STORAGE, the simplified
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12 software, does not take into account K values.
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What about assuming $Hl/p \rightarrow \text{Infinite}$?

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20 Three different situations of the mass transfer coefficient Hl/P are possible:

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22 $Hl/P = 0$: no migration. This value of the parameter can be used in
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24 Multiwise to describe diffusion during storage of empty containers before
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26 packaging foods for non volatile contaminants.
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29 $Hl/P = 1$ ($Hl/P \rightarrow \text{infinite}$): this is the (worst) case generally used; the
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31 partition equilibrium on the surface is instantaneously reached.
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34 $Hl/P > 0$ but low (in the 10^{-11} - 10^{-8} range): in this case, the migration of
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36 the pollutant is partly controlled by its rate of evacuation from interface to food.
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38 Since the prediction of Hl/P values has never been studied in literature, it is
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40 unfortunately not possible to propose a better approach. Assuming $H \rightarrow \text{infinite}$ is
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42 an overestimation, contributing to a worst case approach, but very far from the
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44 behaviour of real viscous foodstuffs.
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What about the partition coefficient at barrier / polymer interface: diffusion and solubility barriers?

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55 The influence on migration of the partition coefficient of the migrant between
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57 polymer layers is illustrated on Figure 11. This is obtained by a simulation using
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MULTIWISE, for a three-layer material, with the contaminant initially located in layer 2, diffusing through the barrier (layer 1) before migrating into food. If the substance has a polarity very different from that of the barrier, its partition coefficient between layers 1 and 2 may change dramatically. In all simulations, the diffusion coefficients in all layers are the same: $D = 4.4 \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, which corresponds to trichloroethane in polypropylene, calculated from the Piringer equation (Begley *et al.* 2005). It is seen that this partition coefficient strongly influences the migration kinetics, but has no influence on the lag time.

This is the case of polar substances, coming from instance from a polar substrate like paper (here layer 3). If the barrier is apolar (like polypropylene), the migration of the polar substance will be kept to a very low level even after the lag time.

This illustrates that numerous possibilities exist to design a functional barrier, by playing on the diffusion behaviour, but also on the partition behaviour between different layers. With $K_{\text{barrier/layer 2}} = 0.01$, the barrier is a very efficient solubility barrier.

CONCLUSION

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In principle, a large set of parameters is needed to assess the efficacy of a functional barrier: diffusion coefficients, activation energy, mass transfer coefficients at the different interfaces and partition coefficients, plasticization parameters.

It is possible to simulate the behaviour of functional barriers, using some assumptions for the parameters.

Parameters which are overestimated:

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

Parameters which have to be determined: h_c

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

Parameters for which there is no value currently available:

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6 The activation energy of diffusion in melted state, E_a , is also a key parameter.
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8 The lower E_a , the larger is the barrier pollution. DMA in different polymers
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10 display very large differences. In PROCESS, these values are used. But the
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12 structure of the migrant probably plays an important role, which has not been
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14 studied up to now. Pending more data, we propose to use an average value $E_a = 50$
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16 kJ mol^{-1} .
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22 The partition coefficients between polymer layers have a very important effect on
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24 migration kinetics, but only a reduced effect on the lag time. In the FAIR project,
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26 we focused on functional barriers linked to restricted diffusion properties. With
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28 such diffusion barriers, the larger the molecular weight of the migrant, the lower
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30 its diffusion coefficient (at least in first approximation) and the larger the barrier
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32 effect. This work also illustrates how functional barriers may work based on
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34 opposite polarities and poor solubility of the migrant in the barrier. Solubility
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36 barriers act in a complementary mechanism, reducing the migration of substances
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38 with extreme polarities. Obviously the latter mechanism is less general, but it may
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40 be useful especially when the identity of the migrant is known.
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48 The examples described illustrate both the multiple effects influencing migration
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50 and how the software given allow to optimise a material in function of all these
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52 parameters. PROCESS and STORAGE, using default values of parameters allow
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54 a quick classification of materials on the basis of the lag phase. If more data are
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6 available, MULTITEMP and MULTIWISE can describe the expected migration
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8 kinetics.
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12 In many cases, however, more realistic data are needed. Using only
13 overestimations of migration or of lag phase may lead to the conclusion that no
14 functional barrier exist, which may be too severe. There is then the need of more
15 accurate determinations of some parameters.
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22 23 24 25 26 27 **ACKNOWLEDGEMENT** 28

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34 for financial support of this work.
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43 44 **Literature** 45 46 47 48

49
50 Baner, A.; Brandsch, J.; Franz, R.; Piringer, O., 1996: The application of a
51 predictive migration model for evaluating the compliance of plastic materials
52 with European food regulations. Food Additives and Contaminants, **13**, 587-601.
53
54

55
56
57 Begley T., Castle L., Feigenbaum A., Franz R., Hinrichs K., Lickly T., Mercea
58
59
60

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48
49
50
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56
57
58
59
60

P., Milana M., O'Brien A., Rebre S., Rijk R., Piringer O., 2005: Evaluation of migration models that might be used in support of regulations for food-contact plastics *Food Additives and Contaminants*, 2005, **22**, 73-90

Dole P., Feigenbaum A. E., de la Cruz C., Pastorelli S., Paseiro P., Hankemeier T., Voulzatis Y., Aucejo S., Saillard P., Papaspyrides C. 2006: Typical diffusion behavior in packaging polymers. Application to functional barriers, accepted in *Food Additives and Contaminants*

Feigenbaum A., Dole P., Aucejo S., Dainelli D., de la Cruz Garcia C., Hankemeier T., N'Gono Y., Papaspyrides C.D., Paseiro P., Pastorelli S., Pavlidou S., Pennarun P.Y., Saillard P., Vidal L., Vitrac O., Voulzatis Y., Functional Barriers: properties and evaluation, *Food Additives and Contaminants*, 2005, **22**, 956-967

Franz, R.; Huber, M.; Piringer, O., 1997: Presentation and experimental verification of a physicomathematical model describing the migration across functional barrier layers into foodstuffs. *Food Additives and Contaminants* **14**, 627-640.

Mougharbel A., Feigenbaum A., Vitrac O.: Interfacial mass transport properties which control the migration of packaging constituents into foodstuffs; submitted to *Journal of Food Engineering*

Pennarun P. Y., Ngonu Y., Dole P., Feigenbaum A., 2004a: Functional barriers in PET recycled bottles. Part II: diffusion of pollutants during processing, *Applied polymer science*, **92**, 2859-2870

1
2
3
4
5
6 Pennarun, P. Y.; Dole, P.; Feigenbaum, A., 2004b: Overestimated diffusion
7 coefficients for the prediction of worst case migration from PET: Application to
8 recycled PET and to functional barriers assessment. *Packaging Technology and*
9 *Science* **17**, 307-320

10
11
12
13
14
15
16 Pennarun P. Y., Dole P., Feigenbaum A., 2004c: - Functional barriers in PET
17 recycled bottles. Part I. Determination of diffusion coefficients in bioriented PET
18 with and without contact with food simulants, *Journal of Applied Polymer*
19 *Science*, **92**, 2845-2858

20
21
22
23
24
25
26 Pennarun P. Y., Dole P., Feigenbaum A., 2005: - Experimental direct evaluation
27 of functional barriers in PET recycled bottles. Comparison of migration
28 behaviour of mono and multilayers, *Packaging Technology and Science*, **18**, 107-
29 123

30
31
32
33
34
35
36 Perou, A. L.; Vergnaud, J. M., 1997: Contaminant transfer during the coextrusion
37 of food packages made of recycled polymer and virgin polymer layers.
38 *Computational and Theoretical Polymer Science*, **7**, 1-6.

39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
Pez-Carballo GL, Cava D., Lagarö JM, Catalá RM, and Gavara R, 2005:
Characterization of the Interaction between Two Food Aroma Components, α -
Pinene and Ethyl Butyrate, and Ethylene-Vinyl Alcohol Copolymer (EVOH)
Packaging Films as a Function of Environmental Humidity, *J. Agric. Food*
Chem., **53**, 7212-7216

Reynier, A.; Dole, P.; Feigenbaum, A., 2002: Migration of additives from
polymers into food simulants: numerical solution of a mathematical model taking

1
2
3
4
5
6 into account food and polymer interactions. Food Additives and Contaminants,
7
8 **19**, 89-102.

9
10
11 Simal-Gandara J.; Sarria-Vidal M.; Rijk R., 2000a: Tests of potential functional
12
13 barriers for laminated multilayer food packages. Part II: Medium molecular
14
15 weight permeants. Food Additives and Contaminants, **17**, 815-819

16
17
18 Simal-Gandara J; Sarria-Vidal M; Koorevaar A; Rijk R, 2000b: Tests of potential
19
20 functional barriers for laminated multilayer food packages. Part I: Low molecular
21
22 weight permeants, Food Additives and Contaminants, **17**, 703-711

23
24
25
26 Vergnaud J.M., 1991, Liquid transport in polymeric materials: modeling and
27
28 industrial applications, Ed. Prentice Hall, Englewood Cliffs, New Jersey, USA.

29
30
31 Widen, H.; Leufven, A.; Nielsen, T. Migration of model contaminants from PET
32
33 bottles: influence of temperature, food simulant and functional barrier. (2004),
34
35 Food Additives & Contaminants **21**(10), 993-1006

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42 **NOTE TO THE REFEREES: 2006 is written for papers accepted,**
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44 **but not yet published. The complete reference will be given at a**
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46 **later stage, when available.**
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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 Dimethoxyacetophenone distribution in a multilayer [EVOH/EVOH-DMA/EVOH] after processing at 210°C

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: Relative functional barrier properties of polymers, at different processing temperatures, thickness needed to maintain $C_{fb} \leq 0.05 C_0$, based on very worst case D (DDMA), calculated with the PROCESS software. Simulated

for $h_c = 255 \text{ W m}^{-2} \text{ s}^{-1}$, relative FB thickness 1/3 of material, and process time $t_e = 0.3 \text{ s}$. Each label mentions polymer type and processing temperature

Figure 6: Migration kinetics at 40°C of trichloroethane from [Virgin PP/polluted PP/Virgin PP (300 μm)] into olive oil and ethanol

Figure 7: Migration kinetics at 40°C of trichloroethane from [Virgin PP/polluted PP/Virgin PP (300 μm)] three-layers into water. The vertical line indicates the lag time with olive oil and with ethanol

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 ($C_{1,t=0} = 0$, $C_{2,t=0} = 0$, $C_{3,t=0} = 500 \text{ mg/kg}$), with $K_{\text{pol1/pol2}} = K_{\text{pol2/pol3}} = 1$, $K_{\text{liquid/pol1}} = 1$; $D_{\text{pol1}} = D_{\text{pol2}} = D_{\text{pol3}} = 4.4 \cdot 10^{-11} \text{ cm}^2 \text{ s}^{-1}$.

Figure 9: Migration kinetics at 40 °C of Benzophenone from [Virgin PP/polluted PP/Virgin PP (300 μm)] three-layers into water.

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

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Figure 11: influence on migration of the partition coefficient between (K_{barrier/pol2}) the barrier and the second layer of a three layer material (250-500-250 μm), 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), with K_{pol2/pol3}=1, K_{liquid/barrier} = 1; D_{pol1} = D_{pol2} = D_{pol3} = 4.3 10⁻⁹ cm² s⁻¹

	D ($10^{-10} \text{ cm}^2 \text{ s}^{-1}$)		
	Moisan test	FB migration experiment (apparent D)	
Simulant →	None ("intrinsic" D)	Ethanol	Olive oil
↓ Surrogate			
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)

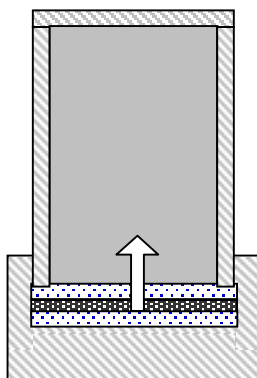


Figure 1: Principle of the migration test: a V/C/V three-layer (Virgin/Contaminated/Virgin) is in contact with the simulant on one side, in a stainless steel cell

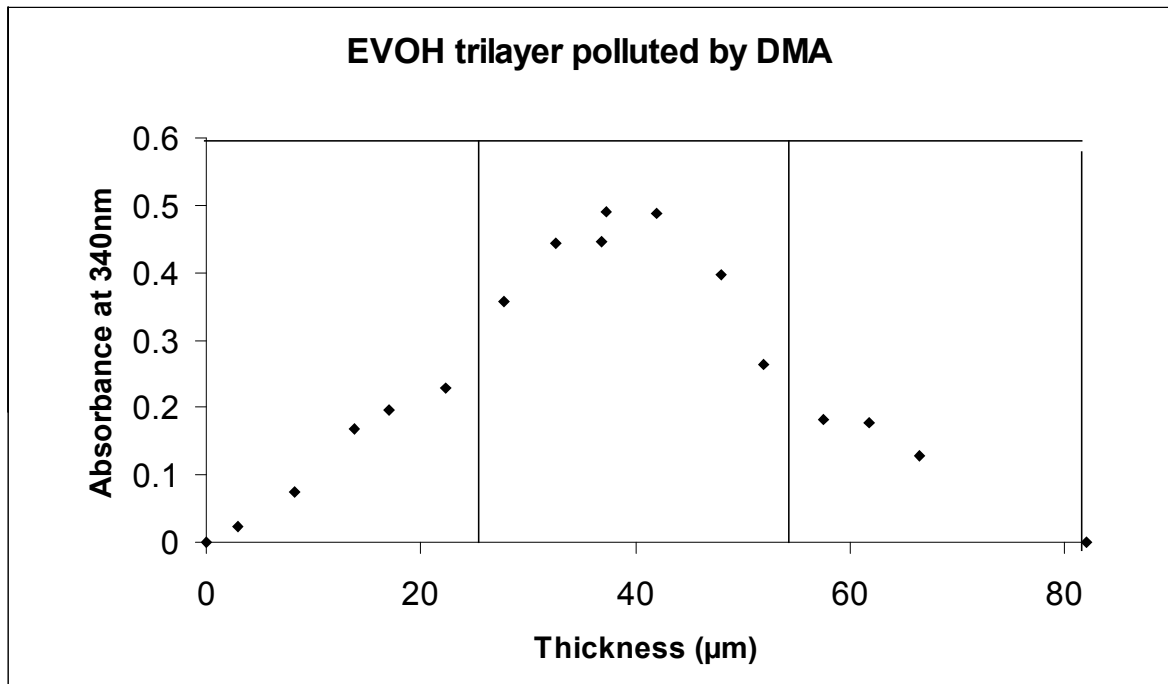


Figure 2: Experimental 2,4-Dimethoxyacetophenone distribution in a multilayer [EVOH/EVOH-DMA/EVOH] after processing at 210°C

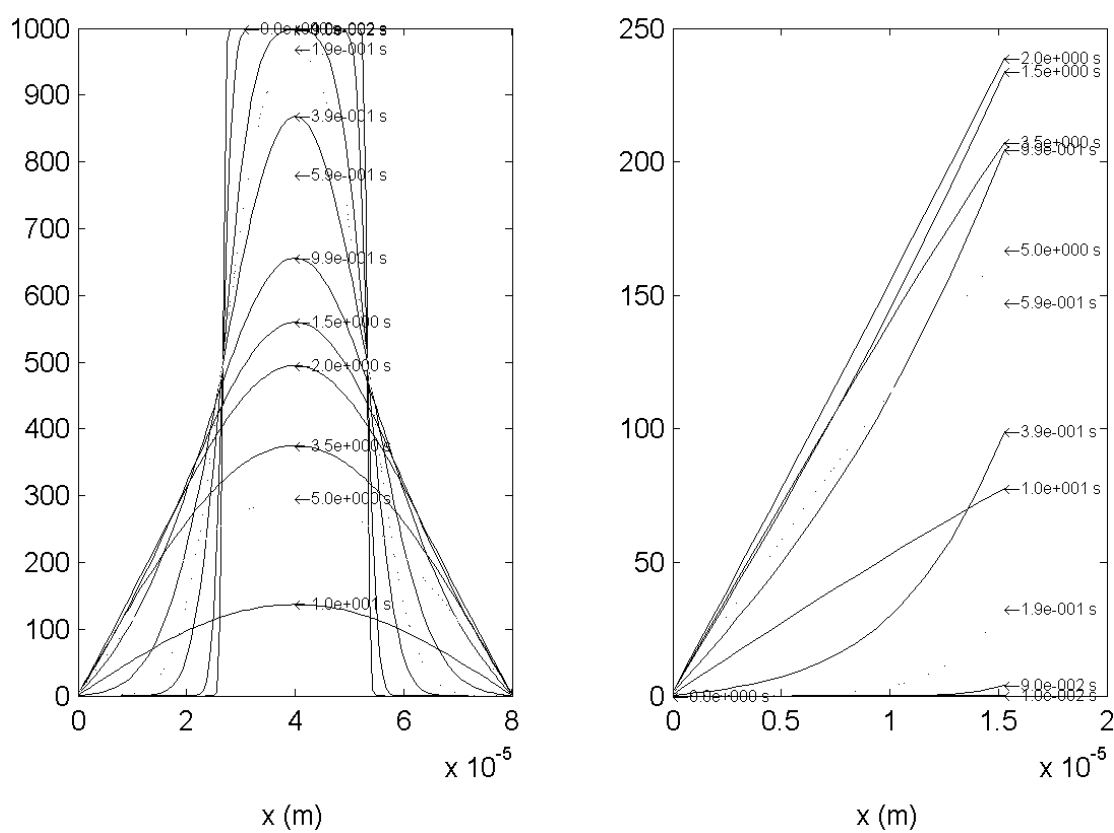


Figure 3: DMA diffusion profile corresponding to an evaporation of the diffusant at the surface with $HP/a = 0.001 \text{ m s}^{-1}$

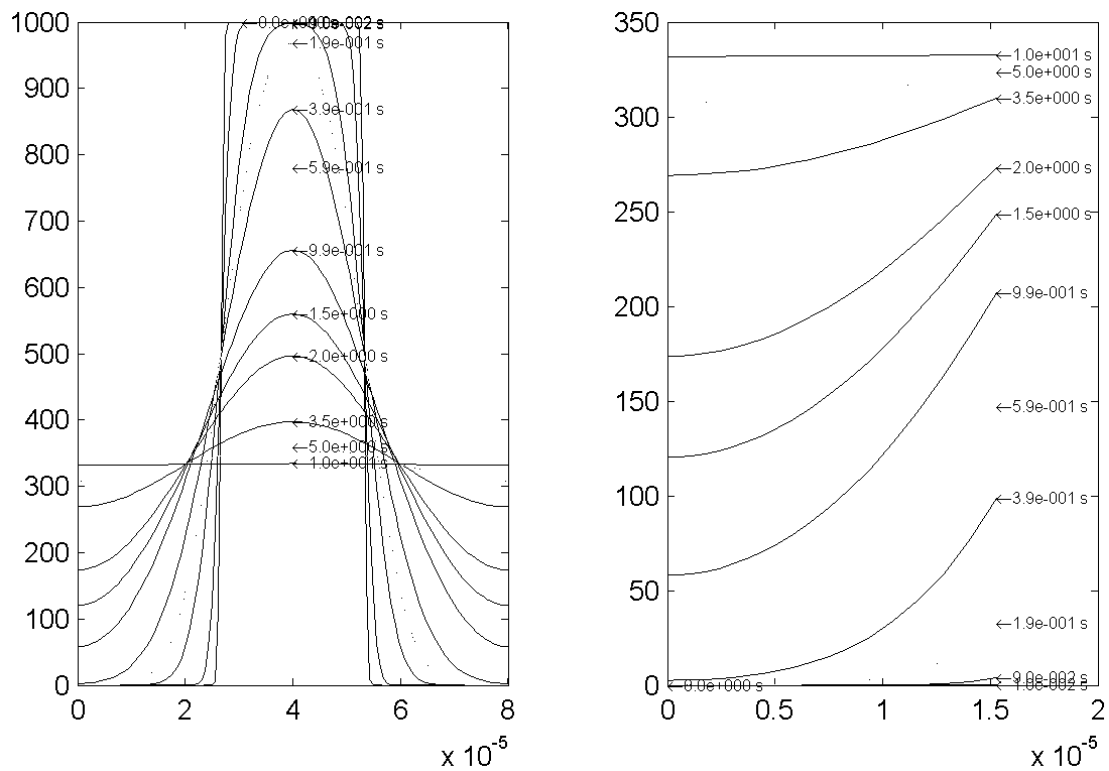


Figure 4: DMA diffusion profiles, assuming no evaporation at the surface ($HP/a = 0 \text{ m s}^{-1}$). Figure on the right is an expansion of the interface region.

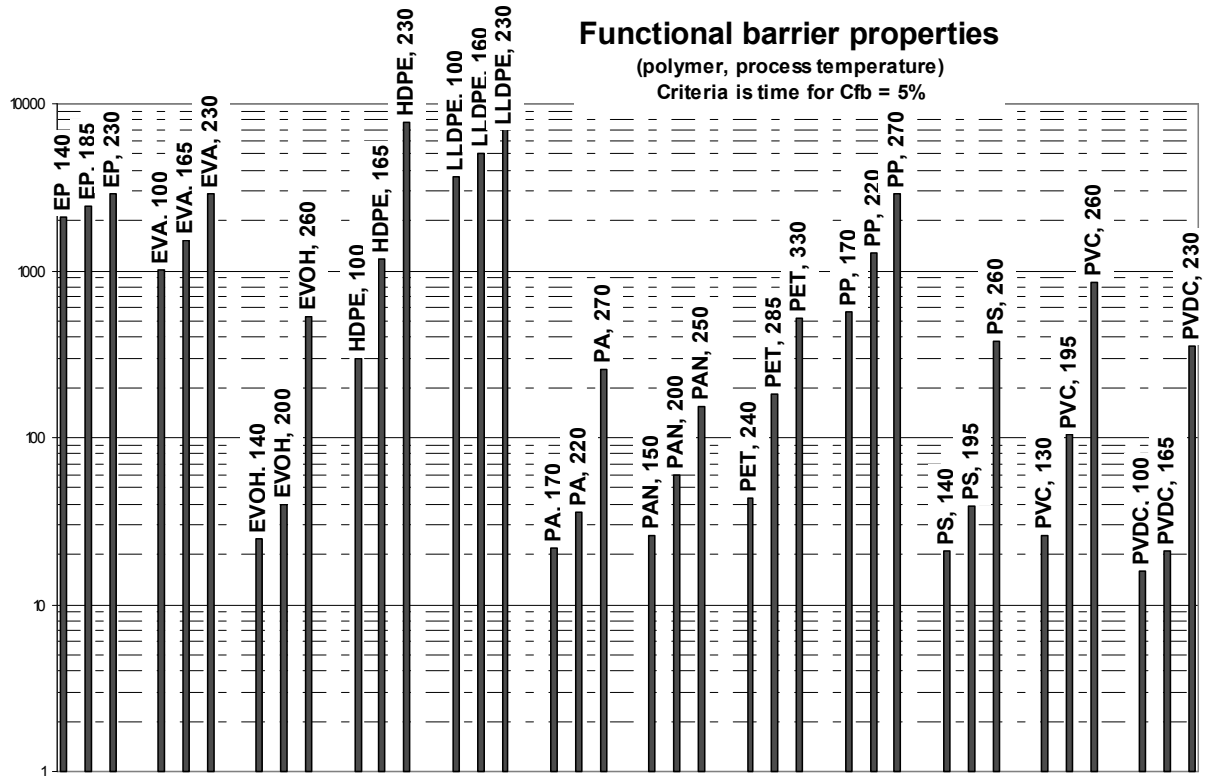


Figure 5: Relative functional barrier properties of polymers, at different processing temperatures, thickness needed to maintain $C_{fb} \leq 0.05 C_0$, based on very worst case D (DDMA), calculated with the PROCESS software. Simulated for $h_c = 255 \text{ W m}^{-2} \text{ s}^{-1}$, relative FB thickness 1/3 of material, and process time $t_e = 0.3 \text{ s}$. Each label mentions polymer type and processing temperature

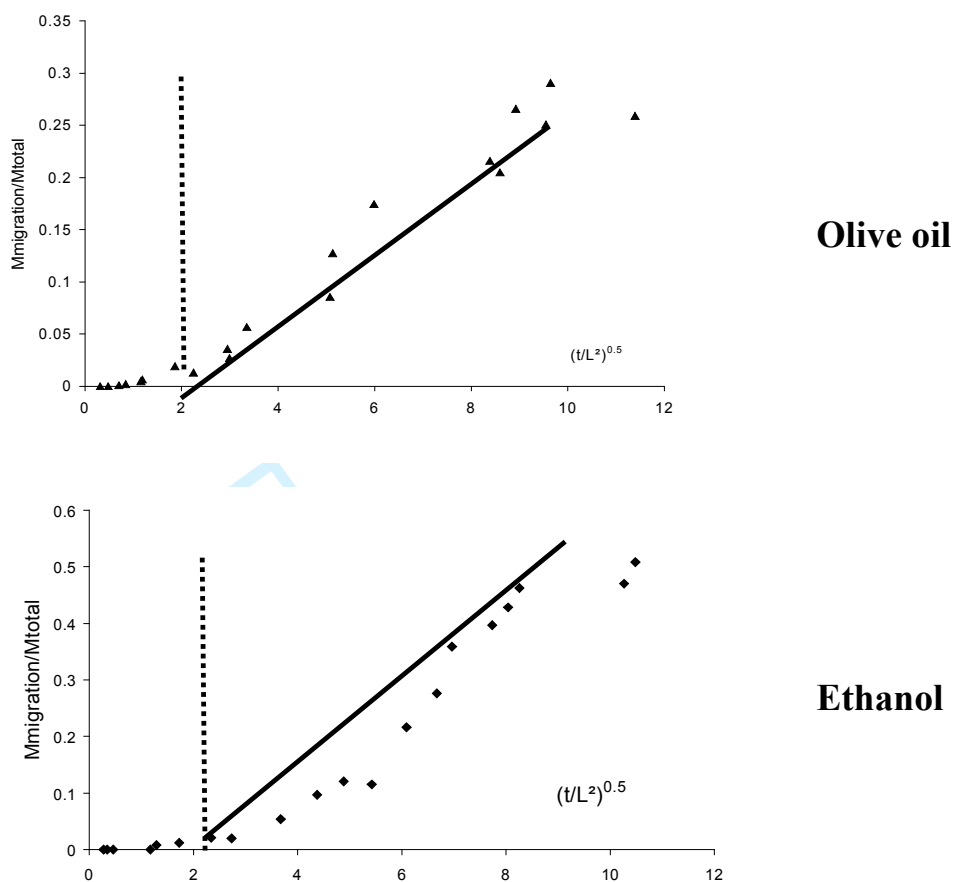


Figure 6: Migration kinetics at 40°C of trichloroethane from [Virgin PP/polluted PP/Virgin PP (300 μm)] into olive oil and ethanol [t in h, L (μm) is the functional barrier layer thickness]

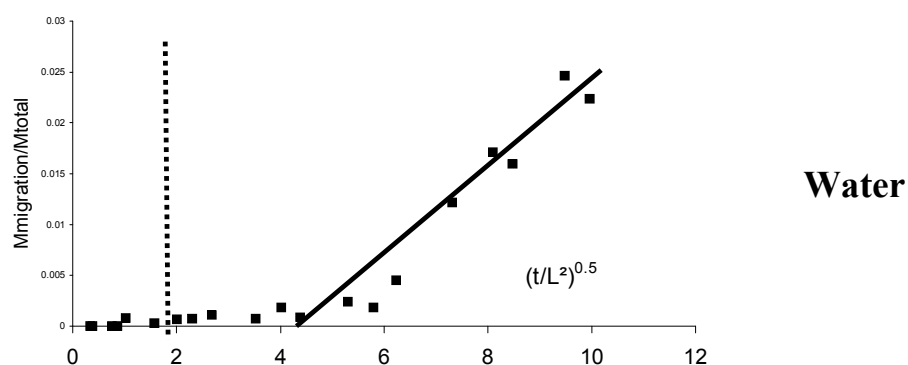


Figure 7: Migration kinetics at 40°C of trichloroethane from [Virgin PP/polluted PP/Virgin PP (300 µm)] three-layers into water. The vertical line indicates the lag time with olive oil and with ethanol [t in h, L (µm) is the functional barrier layer thickness].

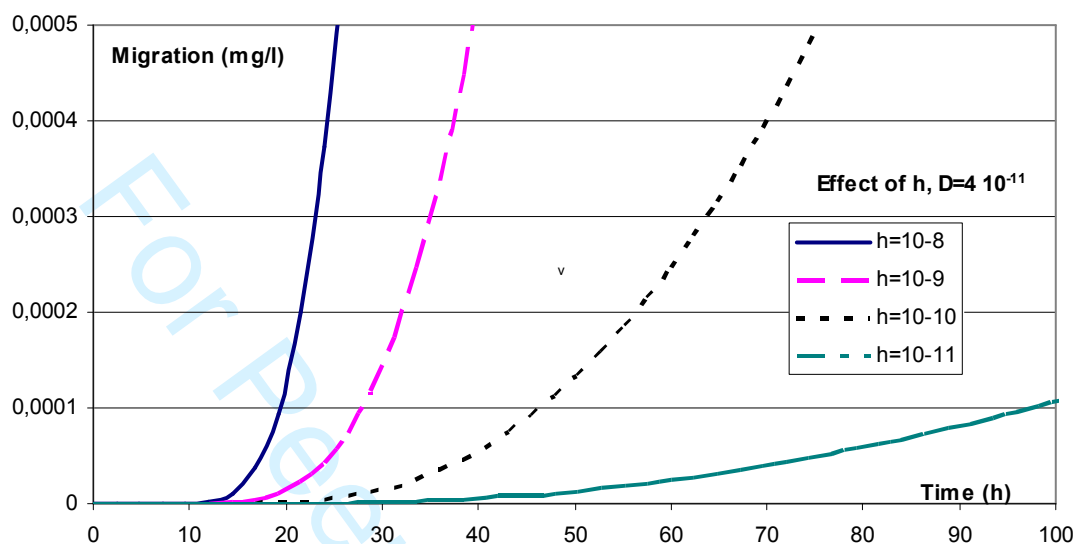


Figure 8: influence on migration kinetics and on lag time of the food/polymer mass transfer coefficient. Calculation made with MULTIWISE, assuming a three layer material (25-50-25 μm), the migrant is initially in layer 3 ($C_{1,t=0} = 0$, $C_{2,t=0} = 0$, $C_{3,t=0} = 500$ ppm), with $K_{\text{pol1/pol2}}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

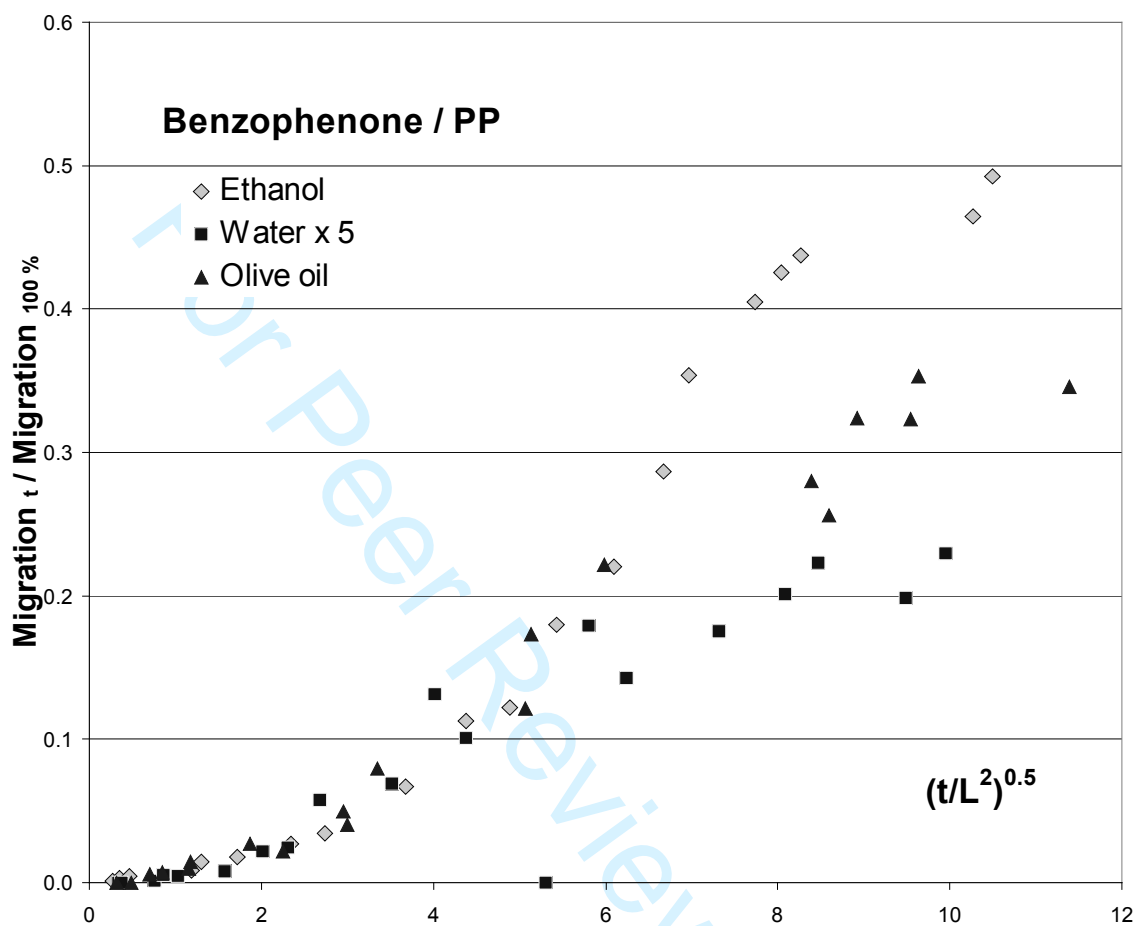


Figure 9: Migration kinetics at 40 °C of Benzophenone from [Virgin PP/polluted PP/Virgin PP (300 μm)] three-layers into water [t in h, L (μm) is the functional barrier layer thickness].

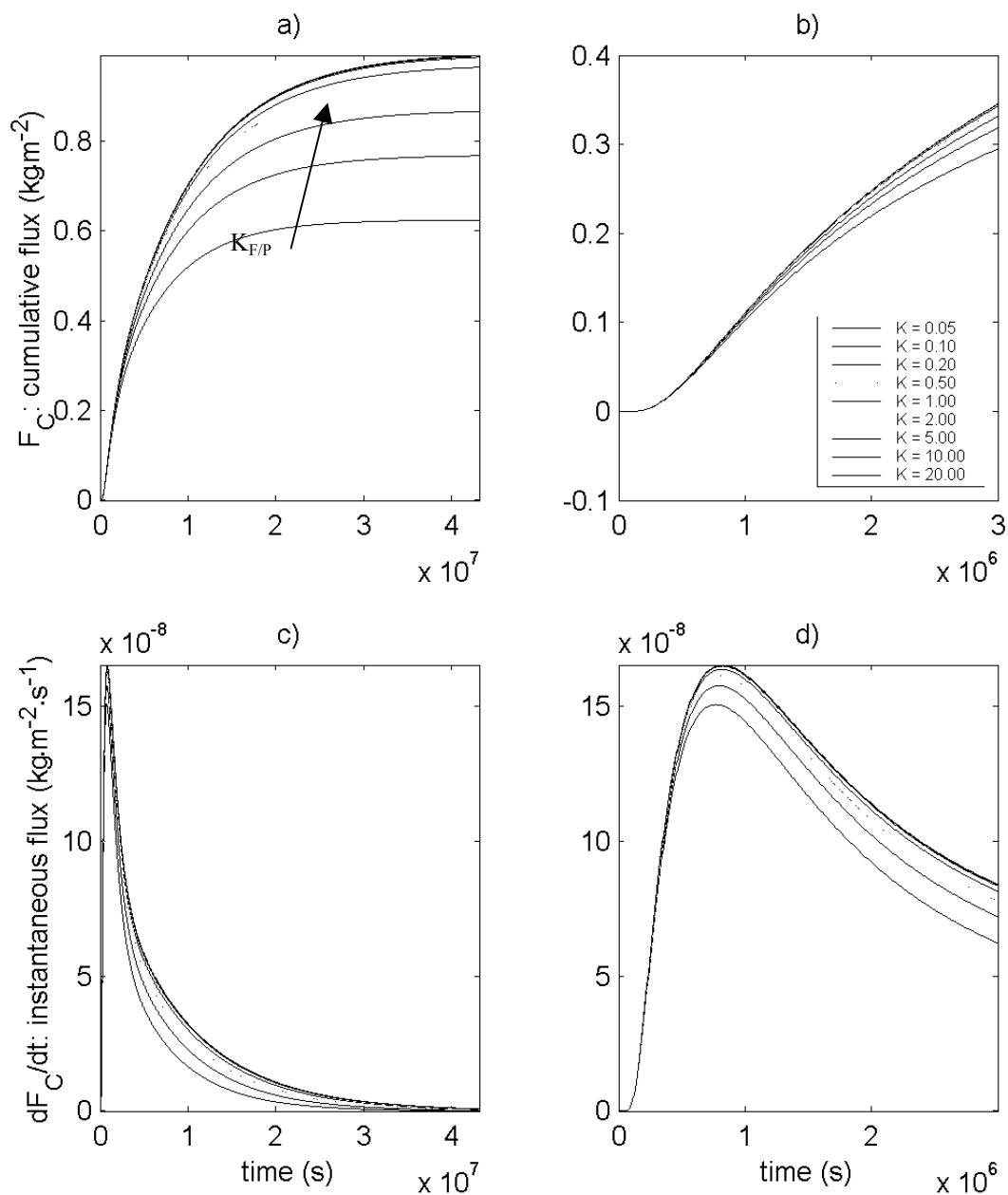


Figure 10: simulation of migration kinetics, using different food/packaging partition coefficients: a, b: F_C = migration (kg m⁻²); c, d: derivative of migration (kg m⁻² s⁻¹)

b and d are enlargements of a and c respectively

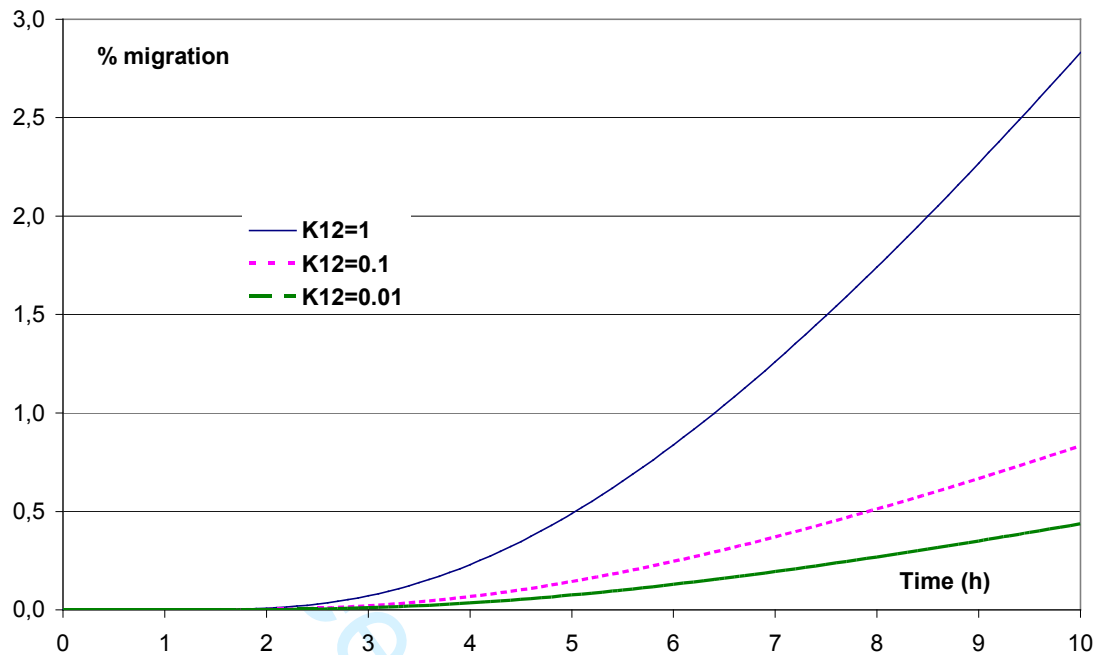


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