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MIGRATION MEASUREMENTS FROM PLASTIC PACKAGING: A SIMULATION STUDY ON INFLUENCE OF INITIAL CONCENTRATION PROFILE

Migration of components from plastic packaging into foodstuffs or into medicines is a very important issue, concerning public health. Using experimental techniques, like gas chromatography-mass spectrometry, these essays measure total migration and specific migration of components from plastic packaging. This work presents an explanation and applications of a numerical technique tool for this measurement, allowing the comprehension of the diffusion process and the estimate of component migration in difficult or impractical measurements. As an application example, the non-uniform influence of initial concentration profile on the migration is presented, demonstrating the necessity of this profile determination for high quality considerations on involved metrology.

Keywords: migration, diffusion, packaging, simulation, chemical contamination.

1. INTRODUCTION

Mathematical models are essential for the comprehension of an uncounted number of phenomena. The execution of the model calculus procedure, called *simulation* of the real experiment, at many different phenomenon conditions, could be considered as an experiment inside computer and, generally, is far less expensive then the experiment itself. Diffusion models for migration measurements in food-packaging interactions fit in this case. Description of the process is made by Fick´s second law which, in one dimension, is:

$$\frac{\partial}{\partial t}C = \frac{\partial}{\partial x}\left(D\frac{\partial}{\partial x}C \right). \tag{1}$$

C is the concentration of the migrant, generally in μg/mL, and is a mathematical function which depends on space and on time (x and t), or it is said $C = C(x, t)$. D is the diffusion coefficient. It is x dependent for many systems. Its quantity is [distance]^2/[time].

The 1-D model is applicable because the packaging is a very thin plane film, usually of 50 μm thickness, and migration essay vessel has a diameter of 1 cm. Migration is mass transfer from the packaging into *food or medicine* (F/M) by sub-microscopic processes caused by a concentration gradient different from zero. This gradient is orthogonal to the surface of the packaging film. Analogous diffusive systems could use the same procedure described here.

As any differential equation, for its solution it is necessary the *initial condition*, which is $C_o = C(x,t=0)$, called here *initial concentration profile*, ICP, and the *contour conditions*. Starting from C_o, C evolves in time, changing its profile, or mathematical form, as function of x. An illustration of this behavior is shown in Fig. 1.

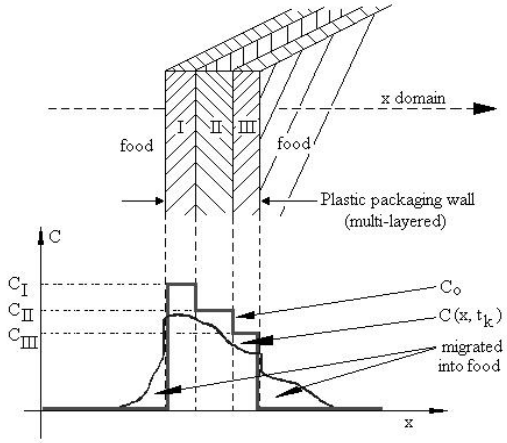

Fig. 1. Above: sketch of a plastic packaging multi-layer system with three wafers: I, II and III. Below: migration occurs into food from both outside layers as in a typical total immersion migration essay. The initial concentration, C_o, is "steps-like" and the concentration profile after a time t_k, $C(x, t_k)$, is indicated. It was not a calculation, it is only illustrative. The area (integrated function) indicated as "migrated into food" is measured in typical migration tests using, as an example, gas chromatography.

Mathematical defined integration of $C(x,t_k)$ in x variable at F/M domain results in the quantity or amount of the migrant which passed to the F/M up to the time t_k. This total amount of migrant as a function of time is the simulation of experimental migration essay, called *migration kinetic*.

When physical media where migration took place (x domain) are non-homogeneous, for the precise resolution of Eq.(1) D must not be considered constant and cannot be put out of the laplacian (second derivative). This is the case when interface(s) is(are) present, as in packaging-F/M systems. For multi-layered plastic packaging this consideration is even more important. It is a common practice to use the *partition coefficient* concept [1] to get round this fact, but the theoretical support for this use is not strong.

Many important models have been proposed and used in migration studies (some examples are in [2-4]). These methods have analytical or numerical solutions, and consider ICP and D as constant averaged values. D is put outside the second derivative in its resolution. This work presents the numerical method for the solution of Eq.(1) and the simulation of systems where C_o and D cannot be homogeneous nor constant in the plastic packaging-F/M system. This is crucial in multilayer packaging systems. Here the influence of the ICP, $C_o(x)$, on the amount migrated into F/M, measured as an application, is presented. ICP could be changed due to weathering, exposure to radiation [5], to chemicals, etc.

2. METHODOLOGY

The numerical solution uses a non-uniform mesh of points for the discretization of x domain. The density of points is higher close to interfaces. The labeling of each point is illustrated in Fig. 2.

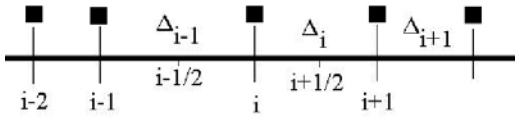

Fig. 2. Non-uniform mesh of points (black squares in figure) used for describe the domain packaging-F/M and their indices. Distances between two points, Δ or Δx, are not always the same, being small close to interfaces

from one medium to another (as between different polymer layers in a multi-layer packaging, or between polymer and F/M).

In order to numerically solve Fick´s equation, Eq. (1), the x domain was discretized in n points by using a three-point finite difference scheme, which generates the following form for the left side of Eq. (1):

$$\begin{aligned}&\frac{d}{dx}D(x)\frac{d}{dx}C(x)\overset{N}{\cong}\frac{d}{dx}D(x)\left[\frac{C_{i+1/2}-C_{i-1/2}}{\Delta_i+\Delta_{i-1}}2\right]=\\&=\left(D_{i+1/2}\frac{C_{i+1}-C_i}{\Delta_i}-D_{i-1/2}\frac{C_i-C_{i-1}}{\Delta_{i-1}}\right)\frac{2}{\Delta_i+\Delta_{i-1}}=\left(\frac{2D_{i+1/2}}{\Delta_i(\Delta_i+\Delta_{i-1})}\right)C_{i+1}+.\\&-\left(\frac{2D_{i+1/2}}{\Delta_i(\Delta_i+\Delta_{i-1})}+\frac{2D_{i-1/2}}{\Delta_{i-1}(\Delta_i+\Delta_{i-1})}\right)C_i+\left(\frac{2D_{i-1/2}}{\Delta_{i-1}(\Delta_i+\Delta_{i-1})}\right)C_{i-1}=OC\end{aligned}\tag{2}$$

Δ_i (or ΔX_i) is the non-constant distance between successive points i. D is diffusion coefficient. Operator O condenses notation.

After some algebraic manipulations of operator O, Eq. (1) becomes:

$$\left(1-\frac{O\Delta t}{2}\right)C_{t+\Delta t}=\left(1+\frac{O\Delta t}{2}\right)C_t=f_i\,.\tag{3}$$

The f_i is a known value, easily calculated, and Δt is the time step.

Opening the O operator, Eq.(3) becomes:

$$C_{t+\Delta t}(x_i)-\Delta t\left[\begin{array}{l}\dfrac{D_{i+1/2}}{\Delta x_i(\Delta x_i+\Delta x_{i-1})}C_{t+\Delta t}(x_{i+1})+\\-\left(\dfrac{D_{i+1/2}}{\Delta x_i(\Delta x_i+\Delta x_{i-1})}+\dfrac{D_{i-1/2}}{\Delta x_{i-1}(\Delta x_i+\Delta x_{i-1})}\right)C_{t+\Delta t}(x_i)+\\+\dfrac{D_{i-1/2}}{\Delta x_{i-1}(\Delta x_i+\Delta x_{i-1})}C_{t+\Delta t}(x_{i-1})\end{array}\right]=f_i.\tag{4}$$

Equation (4) is the time evolution of the Concentration function C. It is a tridiagonal system of n linear equations, where n is the total number of points, which is easily solved by the Thomas algorithm [6].

3. RESULTS/DISCUSSION

Consider generic units for time, [ut], for length (or domain), [us], and for concentration, [C]. Migrated has unit [C].[us]. Typically, [ut] is hour and [us] is micrometer, but it depends on the system.

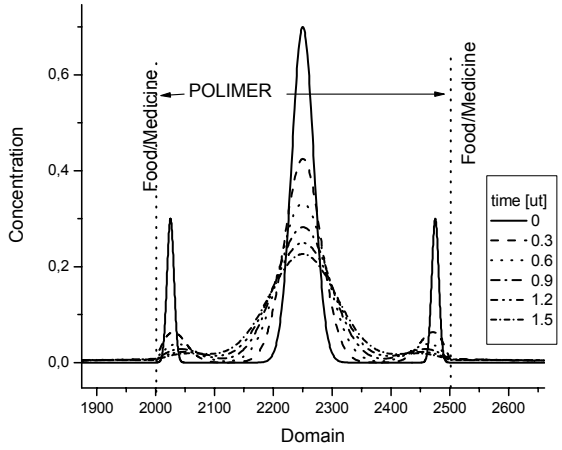

Fig. 3. Changes in concentration profiles, due to diffusion, at indicated times. In this simulation: for polymer, D is $1x10^3$ [us]^2/[ut], and for food/medicine, D is $1x10^5$ [us]^2/[ut].

For a system of monolayer polymer (film of single layer) inside F/M, Fig. 3 shows concentration profiles at six different moments from 0 to 1.5 [ut]. At 0 [ut], the concentration profile, C_o, is a sum of three gaussian functions (triple gaussian). This profile could represent a dispersion of some additive caused by package processing, where near the outside face of the film it had stood with less migrant than the central portion of the film. Figure 4 shows its *migration kinetics*.

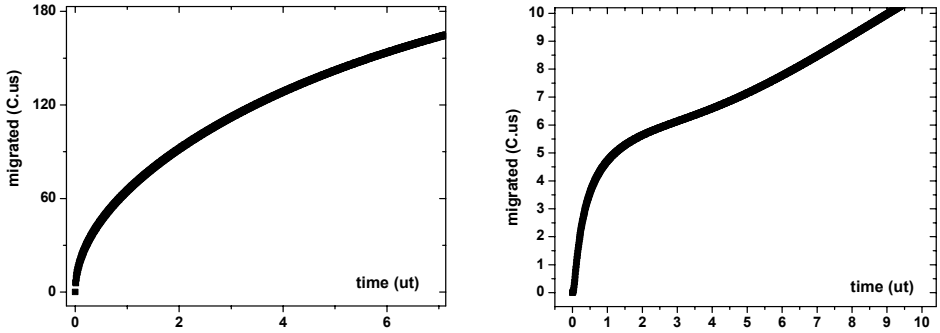

Fig. 4. Migration kinetic simulations. Above, quantity migrated as function of time when C_o is a constant mathematical function (not shown) equal to 1.0 [C] only inside de polymer and zero in F/M.
Below, result for system of Fig. 2. Note the difference in shapes above and below.

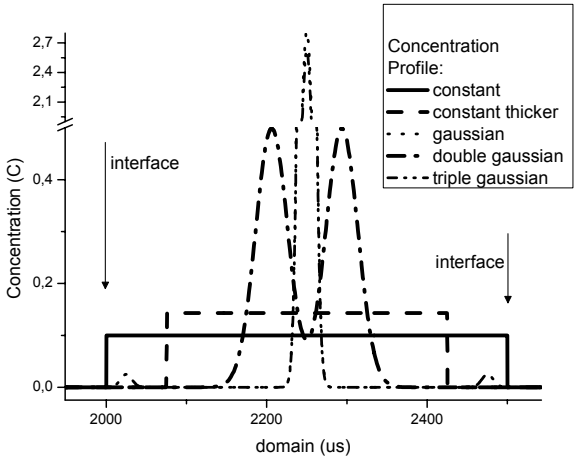

Fig. 5. Initial concentration profiles with the same area or integral value. This integral corresponds to the total amount of migrant inside the polymer. Interfaces between polymer (2000-2500 [us]) and F/M are indicated. Triple gaussian is a profile where the outside gaussian curves are smaller than the central one.

Other simulated systems with different ICPs are presented in Fig. 5. They were designed with the same amount of migrant inside the polymer. Five different C_o functions are shown. We see their very different migration kinetics in Fig. 6. An off-guard researcher would expect that the profiles are the same, based on a real experiment conducted in order to quantify the amount of migrant present inside the polymer before migration. These experiments will result in the same amount for all profiles. The total amount of migrant inside the polymer (TAMP) and the migration kinetic (MK) essays could be measured by gas or liquid chromatography, but it would be very difficult to measure the C_o profile. Determination of the concentration profile at any time is the main relevance of simulation if only one of these essays, TAMP or MK, is available.

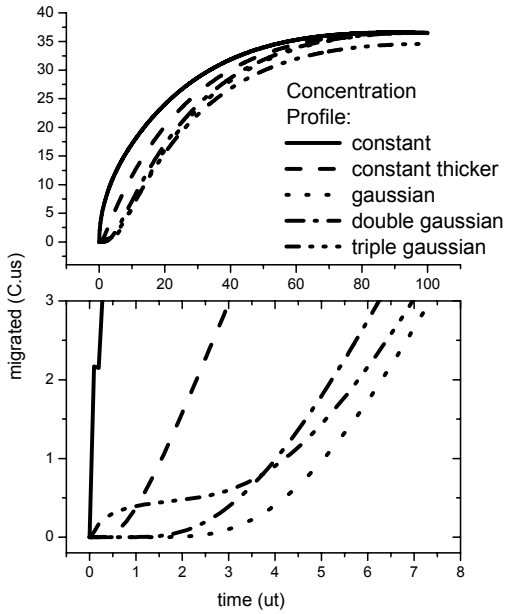

Fig. 6. Migration kinetic simulations for each C_o function shown in Fig. 4. Graphics above and below differ only in scale.

As a practical application, Fig. 7 presents the migration kinetics of Tinuvin P, a U-V radiation absorber additive, from a PET bottle, cut as a small foil and immersed into n-heptane, a food simulant [7]. The agreement of simulation with experiment is very good, and no mathematical model using a constant initial concentration profile could explain the "bump" measured. In this experiment, the amount of this additive migrated did not exceed regulatory boundaries.

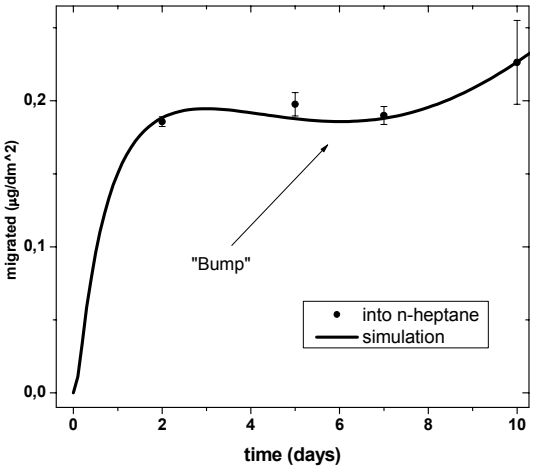

Fig. 7. Experimental results for migration of Tinuvin P into n-heptane and migration kinetic simulation curve (solid) using a triple gaussian C_o profile. Diffusion coefficient of Tinuvin P inside PET was calculated as 4.3×10^2 μm^2/day and inside n-heptane was 5×10^5 μm^2/day.

It is necessary to develop experiments in order to analyze the limits of validity of the proposed simulation, which is not the intention of this paper. Samples with ICPs carefully prepared or special concentration measurement applied to small regions of few micrometers long will be options to evaluate the method.

4. CONCLUSION

It was demonstrated that the *initial concentration profile*, if it is not constant, even in homogeneous monolayer structures, could change the measurement of migrated components from plastic packaging into F/M. The mathematical shape and values of its migration kinetic curve is affected by this initial profile.

If it is not possible to measure this profile precisely, it is important at least to evaluate the influence of this profile variation and to insert it as a source of uncertainty, in the migration measurement method. This simulation method can be used in the determination of this uncertainty component, scanning the input ICP values.

The application of this simulation in experiments like migration of Tinuvin P into n-heptane allows to determine the diffusion coefficient, in case for Tinuvin P inside PET and inside n-heptane. The migration kinetic is better understood.

It can be also used in measurements of limit of shelf life, changes due to temperature, weathering , effects of exposure to radiation , etc.

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