Mathematical Model for the Migration of Thinuvin P from PET Bottles into n-Heptane

José Eduardo Manzoli[1,2,+]
Magali Monteiro[3]

[1]*Centro de Tecnologia das Radiações, CTR - Instituto de Pesquisas Energéticas e Nucleares, IPEN, São Paulo, Brasil, jmanzoli@ipen.br*
[2]*Universidade São Judas Tadeu, São Paulo, Brasil*
[3]*Departamento de Alimentos e Nutrição, Faculdade de Ciências Farmacêuticas, UNESP, Araraquara, Brazil*
+corresponding author

Migration of Tinuvin P, a UV Stabilizer, from PET bottles into foodstuffs is a very important issue, concerning public health. Gas chromatography-mass spectrometry has been used to quantify migration of such a component from the polymeric packaging into food simulants. This work presents an explanation of a numerical technique used to model the Tinuvin P migration into n-heptane, allowing the comprehension of the diffusion process and to estimate migration aspects of difficult or impractical measurements, as the concentration profile of Tinuvin P in the polymer. The non-uniformity of initial concentration profile produces unexpected shape of migration versus time function.

Introduction

This work uses one part of a major work conducted by another group of researchers, who carried out the migration study of Tinuvin P from PET bottles into many simulants. The complete description of the experimental setup, materials and method are shown in reference [1]. Here, the model is applied only to the migration results of Tinuvin P from PET bottles into n-heptane simulant.

Tinuvin P, a ultra-violet (UV) stabilizer, is a plastic additive used in the polymeric matrix of polyethyleneterephthalate (PET) in order to prevent degradation of both food and polymer. Due to the concentration gradient of this stabilizer, diffusion (or migration) process takes place. It is important to evaluate the amount of migrated additive to access the potential health hazard to consumers presented by exposure to this substance.

In the polymer/simulant system, there are two different media where migration takes place: the PET polymer and the n-heptane simulant. So, *diffusion coefficient*, D, can not be supposed to have a constant value.

Traditionally, homogeneous distribution of stabilizer into PET would generate a kinetic behavior shape as shown in figure 1, which presents the amount of Tinuvin P migrated during the contact time. But this is not the case observed in [1], where the real data gave a different shape (figure 2).

So, this work proposes that this non-expected behavior is caused by a non-homogeneous initial concentration profile.

Numerical mathematical modeling of this process was carried out using finite differences in a non-uniform mesh of points. Results indicated that the non homogeneous initial concentration profile is a strong hypothesis to explain this behavior.

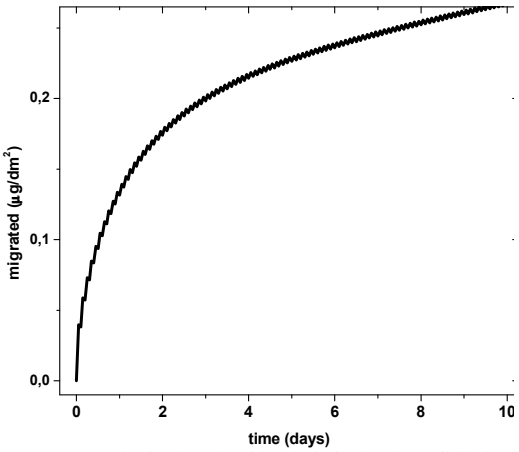

Figure 1 – Typical migration kinetic behavior in a diffusion process where homogeneous initial concentration profile is present. This is a simulation where the initial Tinuvin P concentration is supposed to be uniform (0.3 µg/ml) and PET is 500 µm thick. It was kept in contact with n-heptane up to ten days.

Chemicals and Bottles

Tinuvin P was supplied by Ciba Geigy (Basel, Switzerland). Polyethyleneterephtalate (PET) bottles were supplied by Engepack (São Paulo, Brazil).

Test Samples and Contact

The body section of PET bottles (with and without stabilizers) were cut into pieces of 6 cm^2 (2 x 3 cm^2) of surface area, which weighed 0.2-0.3g each. Each piece was placed in a 20 ml glass vial containing 10 ml of n-

heptane and the vials were hermetically capped. These vials were stored in an oven thermostatically set at 40±1 °C and were taken out for analysis after 2, 5, 7 and 10 day period for the kinetic study. Triplicate samples were analyzed at each time. A blank prepared only with simulant and another with PET without stabilizer, were used as reference, and exposed and analyzed under the same conditions described. All migration tests were carried out by total immersion.

Sample Treatment and Analysis

N-heptane simulant was evaporated after the migration tests in a rotary evaporator to, approximately, 150 µl, and a benzophenone standard solution (300 ng/g) was added as internal standard. These solutions were filtered through PTFE (0.45 µm) filters before injection in the GC/MS system.

Gas Chromatography/Mass Spectrometry

The GC/MS system consisted of a Hewlett-Packard (Palo Alto, CA, USA) 5890 Series II with a 5971-A mass selective detector. A DB 1701 capillary column of 60 m length x 0,25 mm i.d. x 0,25 µm film thickness, and a guard column of 2m length x 0,32 mm i. d. were used. The column temperature was held for 2 min at 100 °C then programmed at 10 °C/min to 280 °C and held for 30 min. Helium was the carrier gas at 110 kPa head pressure. Injections (1 µl) were made at 280 °C. Detection temperature was 280 °C, using SIM mode [2].
Peak areas were measured and the internal standard procedure was used for both calibration and real sample analysis.

Model Methodology

Fick´s (or diffusion) equation in one direction, x, orthogonal to the packaging surface was solved. The numerical solution uses a non-uniform mesh of points for the discretization of this *x* domain. The point density is higher close to the interfaces than in other positions. In order to solve the Fick´s equation numerically, we discretize this differential equation by using a three-point finite difference scheme, which is:

$$\frac{d}{dx}D(x)\frac{d}{dx}C(x) \equiv \left(D_{i+1/2}\frac{C_{i+1}-C_i}{\Delta_i} - D_{i-1/2}\frac{C_i-C_{i-1}}{\Delta_{i-1}}\right)\frac{2}{\Delta_{i-1}+\Delta_i} \qquad (1)$$

Δ is the non-constant distance between successive points *i*.

Equation (1) is a tridiagonal system of n linear equations like (eq.[2]), where n is the total number of points, solved by the Thomas algorithm [3].

Results

If only purely diffusive effects were present, the "bumping" obtained by the experimental data (figure 2) is explained if we consider that some amount of the stabilizer near the surface, migrates first. Then, after some time, another amount deeper in polymer matrix emerges. So, the initial concentration profile shown in figure 3 was proposed. The corresponding kinetics is the solid curve in figure 2.

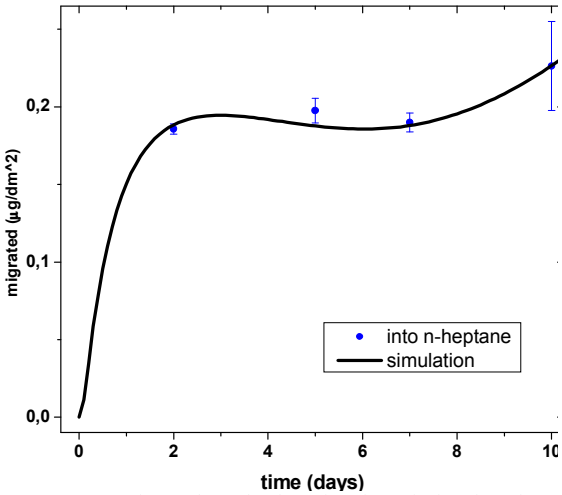

Figure 2 – Experimental results for migration of Tinuvin P into n-heptane [1] and simulated migration kinetic curve (solid). Diffusion coefficient of Tinuvin P inside PET is 4.3 10^2 µm^2/day and inside n-heptane is 5 10^5 µm^2/day.

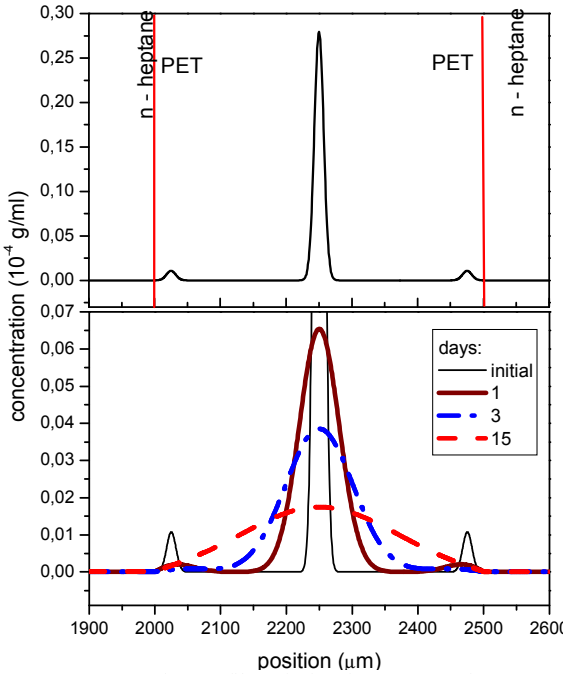

Figure 3 – Concentration profiles of Tinuvin P at some instants as migration happens. Above: proposed initial condition with small amount of Tinuvin P near the interfaces PET/n-heptane and a high quantity in the center of the polymer sheet. Below: profiles after 1, 3 and 15 days of immersion in n-heptane.

Numerical simulations of migration behavior allow the prediction of other food/packaging systems migration, as can be seen in figure 4 and 5.

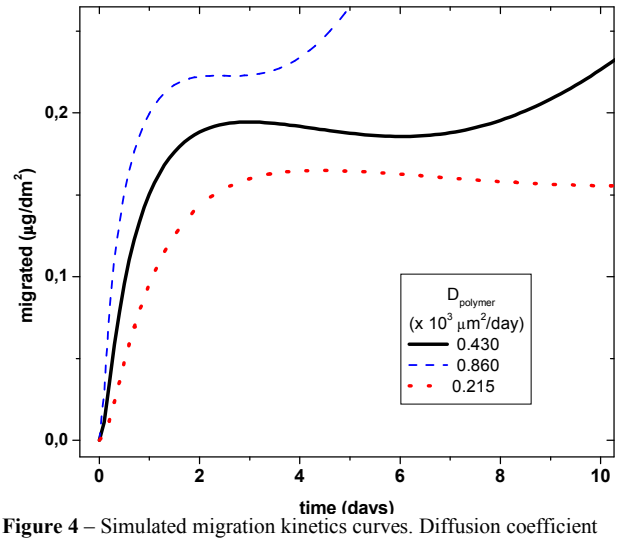

Figure 4 – Simulated migration kinetics curves. Diffusion coefficient of Tinuvin P inside PET was made a double and a half of that one which gave the best fitting value (solid).

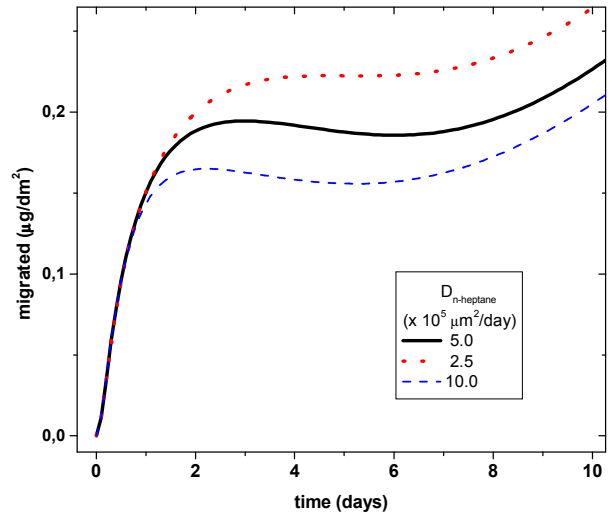

Figure 5 – Simulated migration kinetics curves. Diffusion coefficient of Tinuvin P inside n-heptane was made a double and a half of that one which gave the best fitting value (solid).

Discussion/Conclusion

Obtained simulation curve showed a very good fitting with experimental results. The characteristic bump around the sixth day is very different from traditional diffusion curves. A consequence of this kinetic behavior difference is that predictions of time delayed for the migrated amount to achieve certain values would be significantly different.

References

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