Transfer of Contaminant into Solid Food from a Bottle Made of Bilayer Polymers with a Recycled and a Virgin Layer: Effect of the Thicknesses of These Polymer Layers

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ABSTRACT: The transfer of a contaminant into solid food from a bottle by radial diffusion is considered, when this bottle consists of two polymer layers, one being a recycled polymer, and the other, a virgin polymer. The virgin polymer layer located between the recycled polymer layer and the food plays the role of a functional barrier. The effect of the relative thicknesses of the recycled and the virgin layers on the contaminant transfer is especially studied. The results are expressed in terms of profiles of the concentration of a contaminant developed through the bottle and the food and of the kinetics of a contaminant transferred into the food. The contaminant concentration–time histories are also drawn at various places in the food. Dimensionless parameters are used to obtain results to use in various typical cases. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1291–1301, 1997

INTRODUCTION

Among the various routes of recycling old food packages made of polymers,[1] one consists of reusing them as new food packages. Of course, as potent contaminants may be located in the old food package coming from its previous use, the new food package is made of a bilayer system obtained by coextrusion with a virgin polymer layer placed between the recycled polymer layer and the food.[2–7] Because it takes some time for the contaminant to diffuse through the bilayer package, the virgin polymer layer is considered as a functional barrier, preventing the food from contamination.[8–10] The main problem which arises is to be able to determine the period of time over which the food is protected and to have good knowledge of the parameters which intervene in the process.

Generally, when a polymer is in contact with a liquid, some matter transfers may take place. This process may be simple in a few cases when the liquid alone enters or releases the polymer,[11] or it becomes rather complex when the transfer of the liquid into the polymer is associated with a transfer of additives out of the polymer.[12,13] These transfers are controlled by diffusion, either Fickian when the polymer is in the elastomeric state or non-Fickian when it is in glassy state below the glassy temperature transition T_g.[13]

The problem of reusing an old polymer as a new food package is becoming of great concern in developed countries, and various aspects are covered by legislation.[2–5] A great number of experiments have already been carried out for determining the transport of the contaminant previously located in the recycled polymer by considering the diffusion through the film, and a few of

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them are worth noting: (1) when the thin polymer film was in contact with a very large volume of food and an infinite coefficient of convective transfer at the surface[14–16] and (2) when the thin polymer film was in contact with a finite volume of liquid[17–19]—in this case, the process was described by transient diffusion through the polymer and convection through the liquid with a finite coefficient of mass transfer and calculation was made using a numerical model. Also (3), an attempt was made to develop a mathematical expression coupling the two solutions obtained either with a finite volume of liquid and an infinite coefficient of convective transfer or with an infinite volume of liquid and a finite coefficient of transfer.[20] Generally, these studies were performed using a liquid food.

A few studies were made by considering the radial diffusion in a bottle. A theoretical approach has perhaps laid the way in this case with the radial diffusion of a contaminant through the polymer bottle and the food in a solid state.[21]

One objective in this article was to determine precisely the role played by the functional barrier with respect to the contaminant transfer into the food by considering especially the relative thicknesses of the recycled and the virgin layers. By keeping the thickness of the package constant, the thicknesses of these two polymer layers are varied through a rather wide range, and the transfer of the contaminant is evaluated in these various cases. The results are expressed in three ways: the profiles of concentration of the contaminant developed at various times through the package and the food, this piece of information providing a fuller insight into the nature of the process; the kinetics of the contaminant transfer into the food for various relative thicknesses of the two polymer layers of the package; and the contaminant concentration–time histories at various places in the food.

The other purpose of this study was to build a numerical model taking into account all the known facts considered in a bottle: the radial diffusion of the contaminant through the two layers of the package and through the food with two different diffusivities in the package and the food. This model can be extended to more complex cases: when the contaminant concentration is not initially uniform in the recycled polymer, when a slight evaporation of the contaminant takes place in the surroundings, and when a resistance to transfer exists between the package and the food. The case of a food in a solid state or when highly viscous is considered, with a diffusional transfer.

THEORETICAL

Assumptions

The following assumptions are made in order to make the process clear:

1. Food in a solid state or highly viscous is located in a bottle of radius 5 cm.
2. The bottle consists of two polymer layers: a recycled polymer layer and a virgin polymer layer. The virgin polymer layer is in contact with the food.
3. Transient radial diffusion of the contaminant takes place through the package and the food. The diffusivities are constant either in the package or in the food.
4. Perfect contact exists between the two polymer layers of the package and at the package–food interface.
5. The concentration of the contaminant is initially uniform in the recycled polymer and zero in the virgin polymer.
6. The partition factor at the package–food interface is taken as 1, meaning that the contaminant concentration is the same on both sides of the package–food interface.
7. The contaminant does not evaporate through the external surface of the bottle.

Mathematical Treatment

The radial diffusion with constant diffusivities in the bottle and in the food is expressed by

$$\frac{\partial C_{r,t}}{\partial t} = \frac{D}{r} \cdot \frac{\partial}{\partial r}\left(r \cdot \frac{\partial C_{r,t}}{\partial r} \right) \qquad (1)$$

with the diffusivity D_p in the bottle and D_f in the food, and $C_{r,t}$ is the concentration at time t and radial abscissa r.

The initial conditions are

$$\begin{array}{llll} t = 0 & R_i < r < R_b & C = C_{\text{in}} & \text{recycled layer} \\ & R_f < r < R_i & C = 0 & \text{virgin layer} \\ & 0 < r < R_f & C = 0 & \text{food} \end{array} \qquad (2)$$

The boundary conditions are

- For the external surface of the bottle:

$$t > 0 \quad \frac{\partial C}{\partial r} = 0 \quad r = R_b \tag{3}$$

- For the middle of the food:

$$\frac{\partial C}{\partial r} = 0 \quad r = 0 \tag{4}$$

- For the bottle–food interface:

$$D_f\left(\frac{\partial C}{\partial r}\right) = D_p\left(\frac{\partial C}{\partial r}\right) \quad r = R_f \tag{5}$$

Numerical Analysis

The problem of radial diffusion in the bilayer bottle and the food with the above initial and boundary conditions is resolved by using the Crank–Nicolson method. This numerical model can also be applied in other more complex cases:

1. When the contaminant evaporates at the external surface of the bottle.
2. When a resistance to transfer exists at the bottle–food packaging, by modifying the boundary conditions.

RESULTS

The results obtained by calculation for the contaminant transfer are expressed in three ways: (1) with the profiles of concentration of contaminant developed either in the bilayer package or in the food at various times; (2) with the kinetics of the contaminant transferred into the food; and (3) with the contaminant concentration–time histories at various places in the solid food. Dimensionless numbers are used: $D_p t/L_p^2$ instead of time, with the main characteristics of the package which are the diffusivity and the thickness; the amount of contaminant at time t as a fraction of the corresponding value at equilibrium; and the concentration of the contaminant as a fraction of the initial concentration in the recycled polymer.

Table I Characteristics of the Bottle and Diffusion

Diffusivity (cm^2/s): in the polymer, 10^{-8}; in the food, 10^{-6}
Thickness of the bottle: 0.1 cm
Radius of the food: 5 cm
Various values are used for the ratio of the thicknesses of the two polymer layers of the bottle

Calculations were made by using the values shown in Table I.

Profiles of Contaminant Concentration in the Bottle and the Food for Various Thicknesses of Each Polymer Layer of the Bottle

The profiles of concentration of a contaminant developed either in the bottle or in the solid food are drawn for various thicknesses of each polymer layer of the bottle, by keeping constant the thickness of the bottle at 0.1 cm. The contaminant concentration as a fraction of the initial concentration in the recycled layer is used at various times and places. These curves lead to the following comments:

1. The contaminant diffuses through the bilayer package and through the food. These profiles of concentration in the food shown in Figures 1, 3, 5, 7, and 9 and in the bottle in Figures 2, 4, 6, 8, and 10 give a fuller insight into the nature of the process.
2. At the beginning of the process, for values of $D_p t/L_p^2$ up to 0.01, the concentration at the interface between the two polymer layers falls to $C_{in}/2$, as already found for plane sheets.[22] This is because the thickness of the bottle is very low with regard to its radius.
3. It takes some time for the contaminant to diffuse through the virgin polymer layer which plays the role of a functional barrier. Of course, the following statement holds: The thicker the functional barrier, the longer the period of time over which the food is protected from contamination. This fact clearly appears with the kinetics of contaminant diffusing into the food in Figure 11.
4. On each face of the bottle–food interface, the gradients of concentration are inversely proportional to the diffusivities,

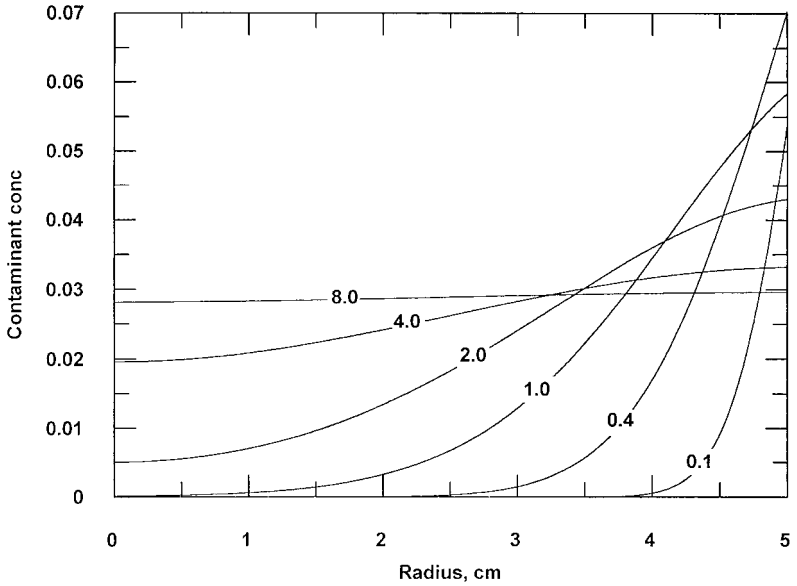

Figure 1 Profiles of concentration of the contaminant developed through the food with the bilayer package of thickness 0.1 cm: recycled layer = 0.075 cm; functional barrier = 0.025 cm; radius of food = 5 cm. $D_p = 10^{-8}$ cm^2/s; $D_f = 10^{-6}$ cm^2/s.

obeying to eq. (5). Thus, in the present case, the gradients of concentration are 100 times lower on the side facing the food than on the other side.

5. The contaminant progresses slowly with time through the food, because of the large value of the radius.
6. At a value of $D_p t/L_p^2$ around 8, the profiles of concentration become rather flat, meaning that equilibrium is nearly reached.

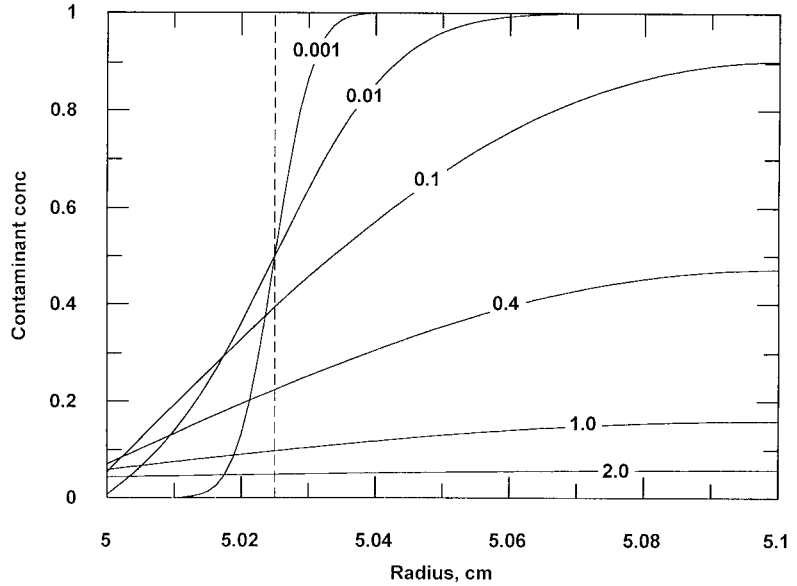

Figure 2 Profiles of concentration of the contaminant developed through the bilayer package of thickness 0.1 cm: recycled layer = 0.075 cm; functional barrier = 0.025 cm; radius of food = 5 cm. $D_p = 10^{-8}$ cm^2/s; $D_f = 10^{-6}$ cm^2/s.

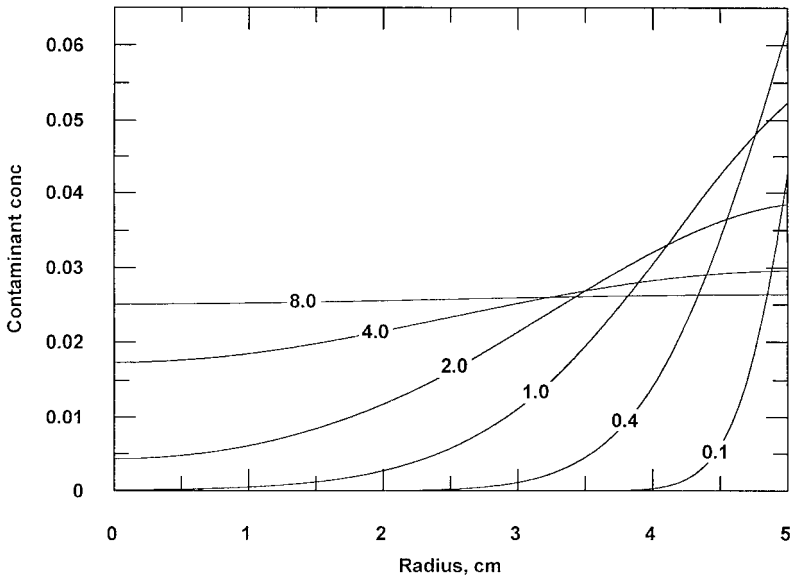

Figure 3 Profiles of concentration of the contaminant developed through the food with the bilayer package of thickness 0.1 cm: recycled layer = 0.066 cm; functional barrier = 0.033 cm; radius of food = 5 cm. $D_p = 10^{-8}$ cm^2/s; $D_f = 10^{-6}$ cm^2/s.

7. At the middle of the food, for $r = 0$, the gradient of concentration is 0, obeying eq. (4).

Kinetics of Transfer of Contaminant into the Food

The kinetics of transfer of a contaminant into the food is drawn in Figure 11 for various values of the ratio of the thicknesses of the recycled polymer and the virgin polymer layers. Dimensionless numbers are used: the amount of contaminant transferred at time t as a fraction of the corresponding amount at equilibrium and $D_p t/L_p^2$ instead of time.

Some conclusions are worth noting:

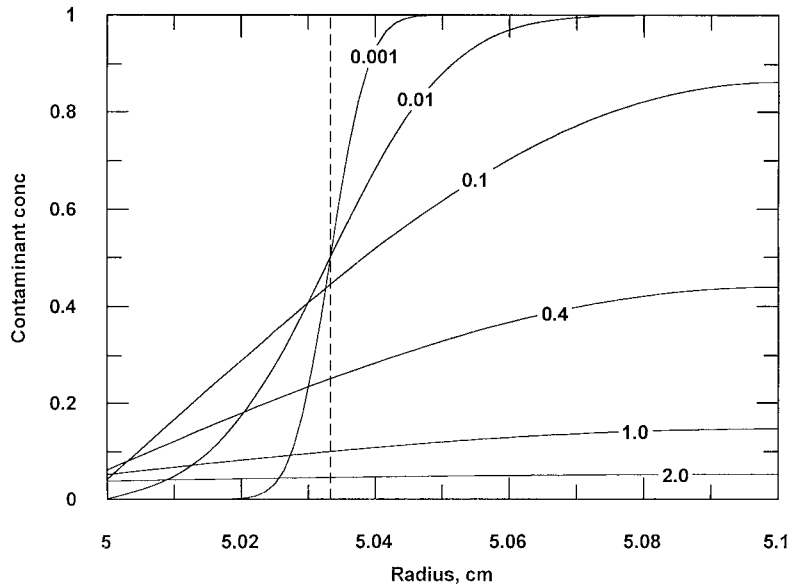

Figure 4 Profiles of concentration of the contaminant developed through the bilayer package of thickness 0.1 cm: recycled layer = 0.066 cm; functional barrier = 0.033 cm; radius of food = 5 cm. $D_p = 10^{-8}$ cm^2/s; $D_f = 10^{-6}$ cm^2/s.

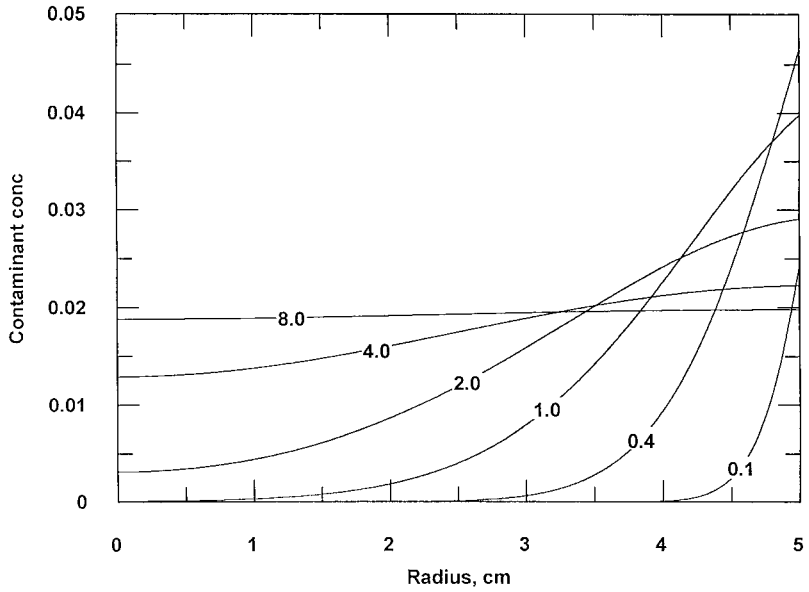

Figure 5 Profiles of concentration of the contaminant developed through the food with the bilayer package of thickness 0.1 cm: recycled layer = 0.05 cm; functional barrier = 0.05 cm; radius of food = 5 cm. $D_p = 10^{-8}$ cm^2/s; $D_f = 10^{-6}$ cm^2/s.

1. The virgin polymer layer acts as a functional barrier, as the kinetic curves of contaminant transfer do not start at the beginning of the process.
2. The time over which the food is prevented from contamination depends on the thickness of this functional barrier. The obvious statement holds: The thicker the functional barrier, the longer the time of protection of the food.

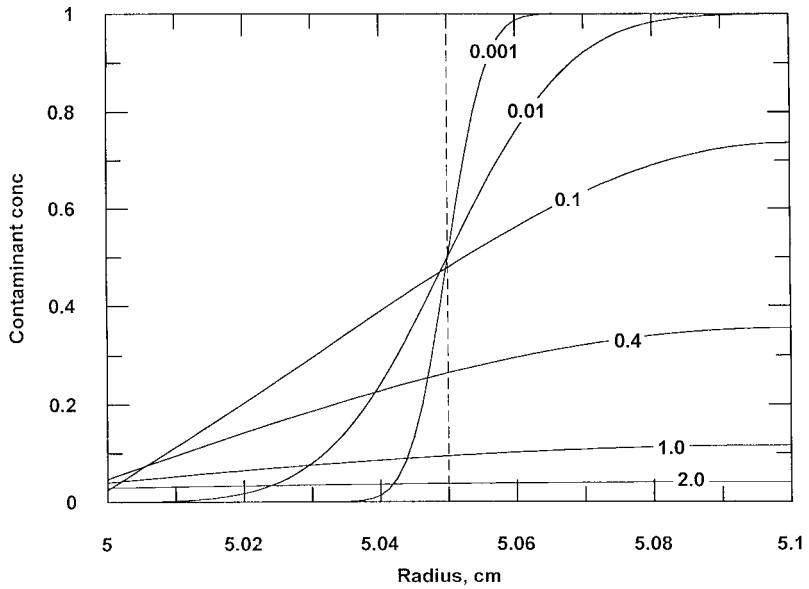

Figure 6 Profiles of concentration of the contaminant developed through the bilayer package of thickness 0.1 cm: recycled layer = 0.05 cm; functional barrier = 0.05 cm; radius of food = 5 cm. $D_p = 10^{-8}$ cm^2/s; $D_f = 10^{-6}$ cm^2/s.

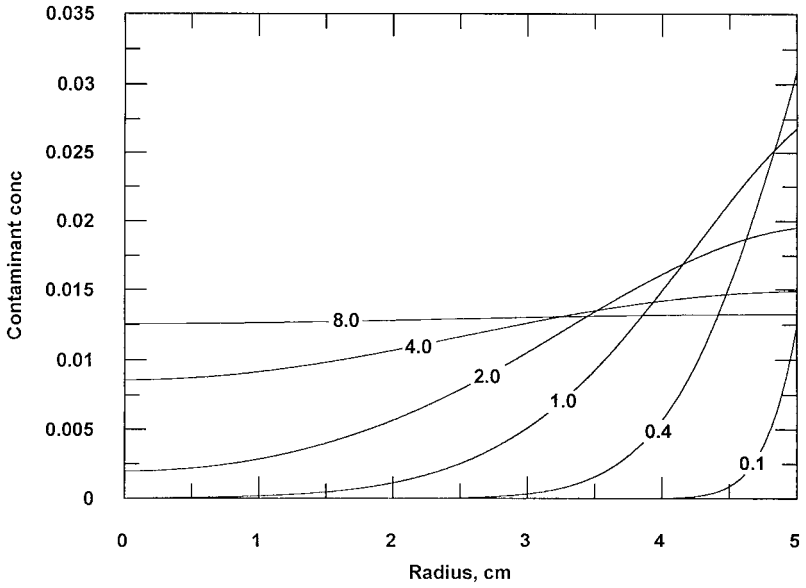

Figure 7 Profiles of concentration of the contaminant developed through the food with the bilayer package of thickness 0.1 cm: recycled layer = 0.033 cm; functional barrier = 0.066 cm; radius of food = 5 cm. $D_p = 10^{-8}$ cm^2/s; $D_f = 10^{-6}$ cm^2/s.

3. The kinetics of the contaminant transfer starts with an horizontal tangent associated with a rate of transfer equal to zero. This rate progressively increases with time.
4. Of course, the thickness of the recycled polymer layer intervenes, as the amount of contaminant is proportional to the volume of this recycled layer. This fact also appears in Figures 1, 3, 5, 7, and 9, where the concentration at equilibrium is given

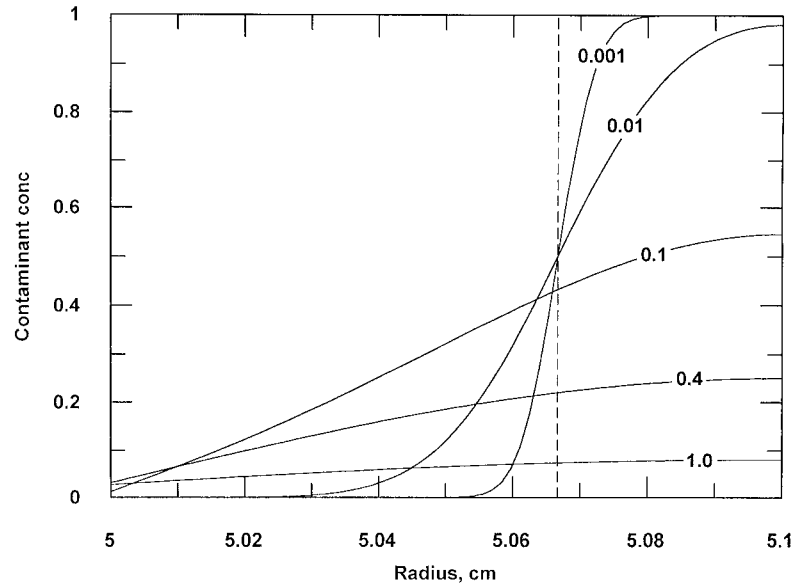

Figure 8 Profiles of concentration of the contaminant developed through the bilayer package of thickness 0.1 cm: recycled layer = 0.033 cm; functional barrier = 0.066 cm; radius of food = 5 cm. $D_p = 10^{-8}$ cm^2/s; $D_f = 10^{-6}$ cm^2/s.

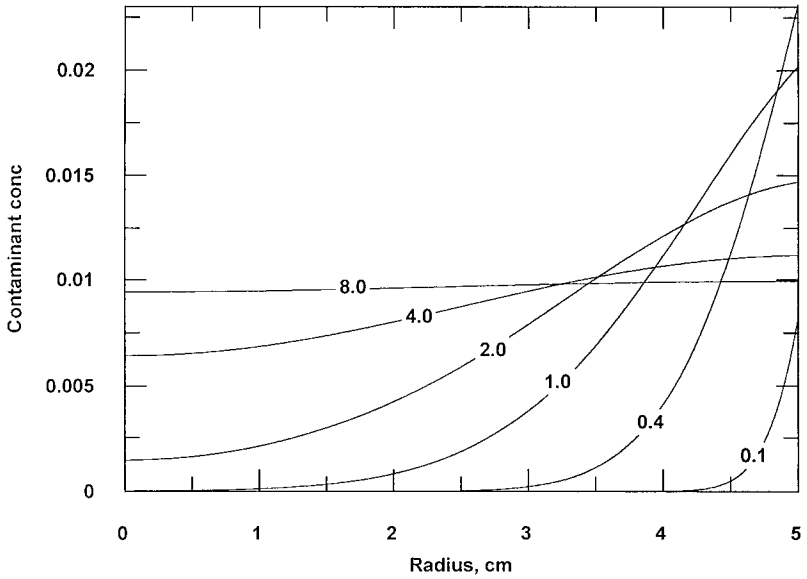

Figure 9 Profiles of concentration of the contaminant developed through the food with the bilayer package of thickness 0.1 cm: recycled layer = 0.025 cm; functional barrier = 0.075 cm; radius of food = 5 cm. $D_p = 10^{-8}$ cm^2/s; $D_f = 10^{-6}$ cm^2/s.

by the obvious relationship

$$\frac{C_{\text{eq}}}{C_{\text{in}}} = \frac{R_b^2 - R_i^2}{R_b^2} \qquad (6)$$

as the partition factor is taken as 1.

Concentration–Time Histories of the Contaminant in Various Places in the Food

With the food being in a solid state, the diffusion of the contaminant is the driving force for the transfer. It stands to reason that the concentration–time histories at various places in the food

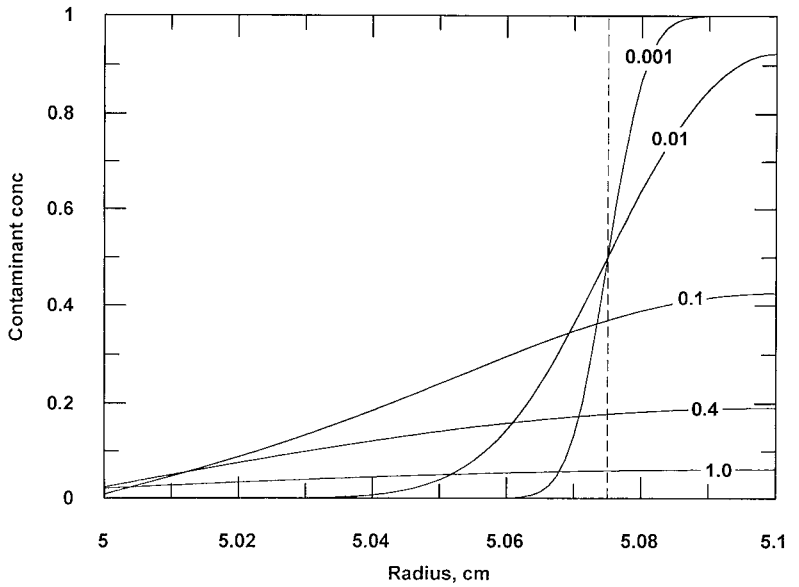

Figure 10 Profiles of concentration of the contaminant developed through the bilayer package of thickness 0.1 cm: recycled layer = 0.025 cm; functional barrier = 0.075 cm; radius of food = 5 cm. $D_p = 10^{-8}$ cm^2/s; $D_f = 10^{-6}$ cm^2/s.

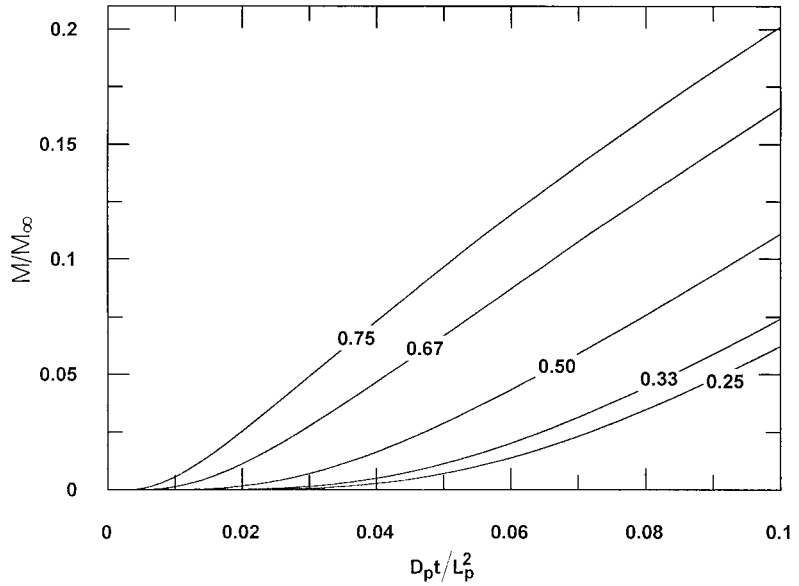

Figure 11 Kinetics of transfer of the contaminant in the food for different values of the ratio of the thicknesses of the recycled layer and the functional barrier (the values are noticed): thickness of the packaging = 0.1 cm; radius of the food = 5 cm. $D_f = 10^{-6}$ cm^2/s; $D_p = 10^{-8}$ cm^2/s.

may be of interest. Two places have been selected, with the middle of the cylindrical food at $r = 0$ (Fig. 12), and the face in contact with the package at R_f (Fig. 13). These histories are drawn for various values of the ratio of the thicknesses of the recycled polymer and the virgin polymer layers.

The following pieces of information were obtained:

1. The concentration–time histories of the contaminant greatly depend on the posi-

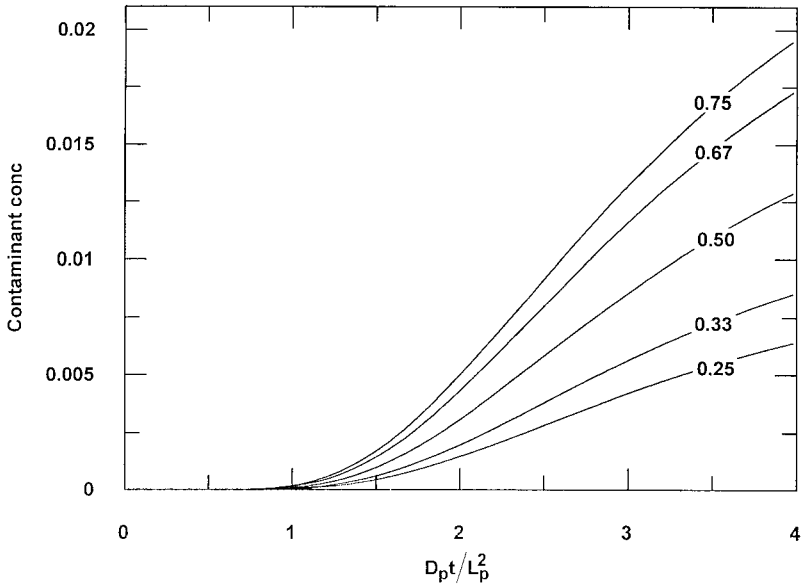

Figure 12 Contaminant concentration–time histories at the middle of the food for various values of the ratio of the thicknesses of the recycled layer and the functional barrier: thickness of the packaging = 0.1 cm; radius of the food = 5 cm. $D_f = 10^{-6}$ cm^2/s; $D_p = 10^{-8}$ cm^2/s.

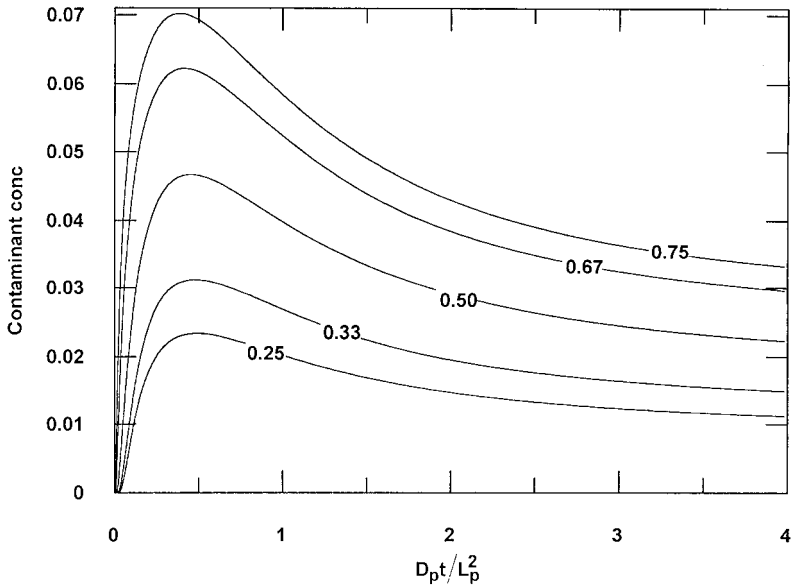

Figure 13 Contaminant concentration–time histories at the surface of the food in contact with the packaging for various values of the ratio of the thicknesses of the recycled layer and the functional barrier (the values are noted): thickness of the packaging = 0.1 cm; radius of the food = 5 cm. $D_f = 10^{-6}$ cm^2/s; $D_p = 10^{-8}$ cm^2/s.

tion in the food when the contaminant diffuses through the food.

2. After a short time of protection, the concentration–time histories in the food at the surface of the bottle increases up to a maximum and than decreases down to equilibrium, as shown in Figure 13.
3. At the middle of the food, the concentration–time histories follow a quite different pattern. After a long period of time associated with D_pt/L_p^2 around 1, the contaminant concentration starts at about the same time, whatever the thickness of the recycled layer, as the contaminant diffuses not only through the bottle but also through the food. After this time, the concentration increases slowly with time up to the equilibrium value. It clearly appears that the concentration at equilibrium depends on the amount of contaminant and on the thickness of the recycled polymer layer.

CONCLUSIONS

For various reasons, it seems to be important to recycle old polymers and perhaps the best way is to recycle old food packages as new food packages. Because of the presence of contaminants located in the old package coming from its previous use, the food may be polluted and a functional barrier is necessary. This functional made of a virgin polymer layer is placed between the recycled polymer layer and the food. As the two polymer layers are coextruded, perfect contact is assumed to be between these layers.

The case of food in a solid state or highly viscous located in a bottle is considered, and the effect of the relative thicknesses of the recycled and the virgin polymer layers on the contaminant transfer in the food is studied by using a theoretical approach. In the present case, the contaminant diffuses not only through the bottle but also through the food.

The results are expressed by the profiles of the concentration of the contaminant developed through the bottle and food system, by the kinetics of contaminant transfer into the food, and by the concentration–time histories at various places in the food. Of course, the relative thickness of the two polymer layers is of great concern. The role of the functional barrier clearly appears in two ways: The food is protected from contamination over a period of time which depends on the thickness of the functional barrier; the rate of contamination after this time of protection increases slowly.

Two kinds of considerations would be taken

into account for selecting the thicknesses of each polymer layer for a given polymer: the economical and the theoretical points of view. As dimensionless numbers are used, and especially $D_p t/L_p^2$ instead of time, the thickness of the layers necessary for a given time of protection could be directly obtained from the master curves for a given contaminant–polymer couple when the diffusivity is known.

LIST OF SYMBOLS

$C_{r,t}$	concentration of contaminant at radial abscissa r and time t
C_{in}	initial uniform concentration of contaminant in the recycled polymer
D_f, D_p	diffusivity (cm^2/s) of the contaminant in the food, in the polymer, respectively
r	radial abscissa
R_f	radius of the food (5 cm)
R_b	radius of the bottle (5.1 cm)
$R_b - R_i$	thickness of the recycled polymer layer
$R_i - R_f$	thickness of the virgin polymer layer
t	time

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