Food Pollution by Bilayer Package with a Recycled Polymer: Effect of Some Parameters

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Abstract: A way of recycling waste polymers consists in reusing them as new food packages. Because of potential contamination, bilayer packages are made with a virgin polymer located between the recycled polymer layer and the food. The virgin polymer layer plays the role of a functional barrier to contamination. Some emphasis is placed on the thickness of each polymer layer by keeping the thickness of the package constant as well as on the volume of food. The process of contaminant transfer is controlled by transient diffusion through the bilayer package and convection into the liquid food. A numerical model, predicting the kinetics of contaminant transfer in the food and the profiles of concentration of contaminant developed through the package, was elaborated. The thickness of the package is 0.03 cm and the volume of food around 730 cm^3. The characteristics are those of polypropylene for packaging and olive oil for food. The effect of the volume of the food in liquid state on the kinetics of transfer is also considered.

INTRODUCTION

For various reasons, an important problem arises with the recycling of waste polymers (Ref. 1). Amongst other ways, such as pyrolysis or combustion, one of them consists in reusing waste polymers as new food packages. But a drawback appears with the potential presence of contaminant in the recycled polymer which can migrate into the food and pollute it (Refs 2,3). Bilayer (or trilayers in sandwich form) packages are thus made with a recycled polymer layer and a virgin polymer layer located in contact with the food. Thus, the virgin polymer layer plays the role of a functional barrier to the pollutant migration (Refs 4-6), and the problem of concern consists in determining the period of time over which the food is protected. Two ways are possible for achieving this determination (Ref. 7): by making experiments which can be tedious and highly time-consuming and by constructing numerical models.

Many experimental studies have been performed considering the diffusion of the pollutant through the polymer and convection into the food (Refs 8-12). Generally, the following assumptions were made: the simultaneous transfer of the food into the polymer is neglected, the diffusion coefficient is constant, the coefficient of convective transfer into the food is infinite, and the volume of the food is infinite. A particular study was made by considering the diffusion of a substance from a polymer into a bath system of finite volume (Ref. 13). Experiments have also been made for evaluating the efficiency of the functional barrier (Refs 14-20). In fact, a great number of studies have been made on the subject of mass transfer between a polymer and liquid food. A literature survey is of interest (Ref. 21).

A theoretical approach was developed for moisture transport through a polymer package into a food by considering the stages of absorption and diffusion (Ref. 22). The process of contaminant transfer is

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rather complex, as it is controlled by transient diffusion through the package and by convection with a finite coefficient of convective transfer into the food of finite volume. Under these circumstances, there is no analytical solution to the problem (Refs 7,23), in spite of an attempt at mixing two analytical solutions (Ref. 13) and the solution must be sought by using numerical methods with finite differences (Refs 7,24). Generally, the problem is far from being so simple (Ref. 7). A double transfer may take place with the liquid entering the polymer, enhancing the release of the contaminant (Refs 7,25). Moreover, as shown recently, the contaminant transfer already starts during the processing of the bilayer polymer system either obtained by blowing extrusion (Ref. 26) or thermoforming (Ref. 27), leading to bilayer packages where a profile of concentration of contaminant exists at the bilayer interface.

The first purpose of this paper is to deeply describe the process of transport of a contaminant through a bilayer package into a finite volume of liquid. A numerical model is thus constructed, taking into account the following stages: diffusion of the contaminant through the package, and convection with a finite coefficient of convective transport into the food. A few assumptions are made in order to simplify the problem, viz., no evaporation of contaminant takes place into the ambience through the outer surface of the package, the diffusion coefficient is constant (it often appears when the concentration of the substance is low) (Refs 7,23), the transfer of the contaminant is only considered (neglecting that of the food into the polymer), perfect contact is obtained at the two polymer interface (which is true as the package layers are coextruded), and the profile of contaminant at the bilayer interface is vertical (meaning that the transfer during the processing is neglected).

The other objective of this study is to determine precisely the effect of the thickness of the recycled polymer layer, by keeping the total thickness of the package constant. The volume of the liquid is 1.5 cm^3/cm^2 of package which corresponds to a cube of 729 cm^3. The values of the diffusion coefficient and the coefficient of convective transfer are taken from a recent study made with polypropylene and olive oil (Ref. 28). For investigating the effect of the volume of food on the kinetics of contaminant transfer, the volume of food is varied from 216 cm^3 to 1728 cm^3, which corresponds to the package volumes of 1 cm^3/cm^2 and 2 cm^3/cm^2 in contact with food, respectively.

THEORETICAL

Assumptions

The following assumptions are made in order to clarify the process.

(i) The bilayer package is made of a recycled polymer and a virgin polymer layer. They are in perfect contact, and are of the same nature, with the same diffusion coefficient.

(ii) The contaminant is initially located in the recycled polymer with a uniform concentration.

(iii) The contaminant transfer is controlled by the Fickian diffusion through the package with a constant diffusion coefficient and by convection into the liquid food with a finite coefficient of transfer. The contaminant does not evaporate through the outer surface of the package.

(iv) There is no food transfer into the package.

(v) The volume of the food is finite.

(vi) The total thickness of the package is kept constant at 0.03 cm. The ratio of the thicknesses of the virgin and recycled layer varies from 0 to 2/3.

Mathematical treatment

The unidirectional diffusion through the thickness of the package is expressed by the Fickian equation with constant diffusion coefficient D.

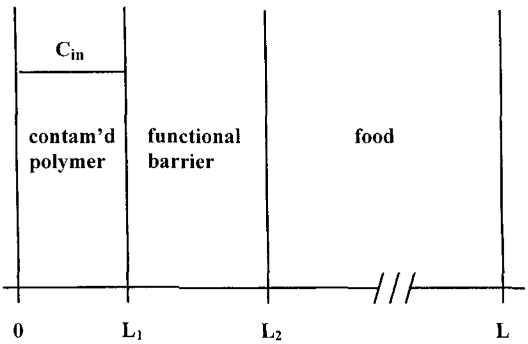
$$\frac{\partial C_{x,t}}{\partial t} = D\frac{\partial^2 C_{x,t}}{\partial x^2} \qquad (1)$$

where $C_{x,t}$ is the contaminant concentration at position x and time t.

The initial conditions are (Fig. 1):

$$t = 0 \qquad 0 < x < L_1 \qquad C = C_{in} \qquad (2a)$$

$$L_1 < x < L \qquad C = 0 \qquad (2b)$$



Because of the convective transport into and through the liquid food, the concentration of the contaminant in the food is always uniform. The ratio of the thicknesses of the polymer sheet and liquid can thus be represented by the ratio of the volumes of the polymer and liquid. The length ($L-L_2$) thus expresses the volume of liquid per unit area of polymer - liquid interface (cm^3/cm^2).

The *boundary conditions are* :

$$t > 0 \qquad x = 0 \qquad \frac{\partial C}{\partial x} = 0 \quad \text{no transfer} \qquad (3a)$$

$$x = L_2 \qquad -D\frac{\partial C}{\partial x} = h\left(C_{L_2} - K.C_l\right) \qquad (3b)$$

Equation 3b expresses the fact that the rate of convective transfer into the liquid is constantly equal to the rate at which the contaminant is brought to the polymer surface by diffusion.

The partition factor K is the ratio of the contaminant concentrations on the polymer surface and in liquid in equilibrium. It is assumed that K is constant at any time (Refs 7,23).

$$K = \frac{C_{L,eq}}{C_{l,eq}} = \frac{C_{L,t}}{C_{l,t}} \qquad (4)$$

Numerical treatment

The problem is resolved by using a numerical method with finite differences (Refs 7,24,25) as the mathematical treatment is not feasible (Refs 7,23). The thickness of the package L_2 is divided into N slices being associated with the integer n.

The new concentration within the slice n after elapsing of time Δt, CN_n, can be expressed in terms of the previous concentrations at the same and adjacent slices. It is obtained:

– Within the package, with 1 < n < N-1

$$CN_n = \frac{1}{M}\left[C_{n-1} + (M-2)\,C_n + C_{n+1}\right] \tag{5}$$

with the dimensionless number M

$$M = \frac{(\Delta x)^2}{D.\Delta t} \tag{6}$$

and the increments of space Δx and time Δt.

– At the package-food interface, with n=N

$$CN_N = \frac{1}{M}\left[2\,C_{N-1} + (M-2-2P)\,C_N + 2\,P.K.C_l\right] \tag{7}$$

with the dimensionless number P

$$P = \frac{h.\Delta x}{D} \tag{8}$$

– On the external surface of the package facing air, with n=0

$$CN_0 = \frac{1}{M}\left[2\,C_1 + (M-2)\,C_0\right] \tag{9}$$

The concentration of contaminant in the food, $C_{l,t}$ increases with time

$$C_{l,t} = \frac{M_t}{V_f} \tag{10}$$

where M_t is the amount of contaminant transferred in the food until time t per unit of the package and V_f is the volume of liquid per unit area of the package.

The amount of contaminant transferred into the food at time t, per unit area, is obtained by integrating with respect to space the concentrations in the polymer at this time:

$$M_t = L_2.C_{in} - \Delta x\left[\sum_{n=1}^{N-1} C_{n,t} + \tfrac{1}{2}\left(C_0 + C_N\right)\right] \tag{11}$$

RESULTS

Some emphasis is placed upon the effect of the functional barrier, and hence the thickness of this virgin polymer layer is varied from 0 to two thirds of the thickness of the package, the latter being kept constant at 0.03 cm. The following values of the ratio of the thicknesses of the virgin and recycled layer are thus considered: 0, 1/3, 1/2 and 2/3. The effect of the volume of the food is also considered, being varied within a rather large range.

The results concern the following: the profiles of concentration of contaminant developed throughout the package at various times; the kinetics of contaminant transferred into the liquid food if the volume of food is 1.5 cm^3/cm^2 of the package - food interface (the volume of a cubic package is 729 cm^3); the time necessary for a given transfer of contaminant into the food to take place; the kinetics of transfer for various volumes of food (shown in Table1).

Dimensionless numbers are used in order to obtain master curves which can be of interest in various cases: the ratio $D.t/L_2^2$ is used instead of time (Refs 7,23); the ratio $h.L_2/D$ is used for characterizing the relative effect of diffusion and convection; the position is expressed by x/L; the concentration in the package is expressed as a fraction of the initial concentration in the recycled polymer $C_{x,t}/C_{in}$; the amount of contaminant transferred into the food at time t is also expressed as a fraction of the initial amount located in the package M_t/M_{in}. The values used for calculation are shown in Table 1.

Table 1: Characteristics used for calculation

Thickness of the package	0.03 cm
Thickness of the functional barrier	0, 0.01, 0.015, 0.02 cm
Volume of the food	216 cm^3 (1 cm^3/cm^2 of package), 729 cm^3 (1.5 cm^3/cm^2 of package), 1728 cm^3 (2 cm^3/cm^2 of package) $D = 7 \times 10^{-11}$ cm^2/s, $h = 10^{-8}$ cm/s, K = 1

The profiles of concentration of the contaminant developed through the various packages are drawn at various times or, rather, at various values of Dt/L_2^2 in Fig. 2a, where the thickness of the virgin polymer layer is 0, in Fig. 2b, where the thickness of the virgin polymer is 0.02 cm, in Fig. 2c, where the thickness is 0.015 cm of both the virgin polymer and recycled polymer layers, and in Fig. 2d, where the thickness of the virgin polymer layer is 0.02 cm. In all cases the volume of food is 1.5 cm^3/cm^2 of package.

The curves in Figs 2a-2d lead to the following comments:

(i) The profiles of concentration developed through the thickness of the packages bring a fuller insight into the nature of the process of diffusion - convection.

(ii) In all cases, the concentration at the polymer surface in contact with the food decreases slowly with time. This fact results from the finite value of the coefficient of convective transfer in Eqs 3b and 7 (Refs 7,23).

(iii) A comparison of the profiles drawn in Figs 2a-2d shows clearly the effect of the functional barrier. With no functional barrier (Fig. 2a), the contaminant enters the food as soon as the process starts. In the presence of a functional barrier, the contaminant first diffuses through the two layers of the package before reaching the food, and thus it takes some time for the contaminant to reach the food.

(iv) It clearly appears that the time necessary for the contaminant to reach the food (which is also the period of time over which the food is protected from contamination) increases with the thickness of the function barrier.

(v) Moreover, another fact of interest appears by comparing the profiles drawn in Fig. 2a, with no functional barrier with the profiles drawn in Figs 2b,c,d. If the recycled layer is in contact with the food, the concentration at the polymer surface is very high in the beginning, and decreases slowly with time. In the case of a bilayer package, the concentration of contaminant on the polymer surface in contact with the food is zero from the beginning of the process until a certain time, and after that, it increases very slowly with time.

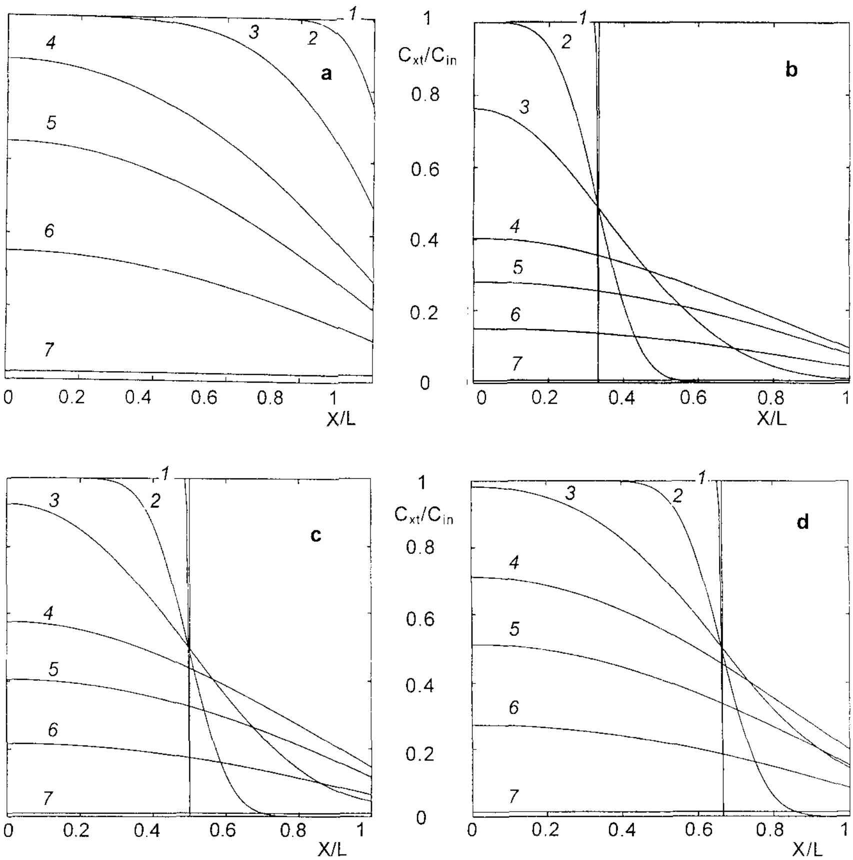


Fig. 2. Concentration profiles of contaminant through the package made of polymer layers for various times (values of Dt/L_2^2 are indicated). Volume of food = 1.5 cm^3/cm^2.

(a) recycled polymer layer 0.03 cm, (b) recycled polymer layer 0.01 cm, virgin polymer layer 0.02 cm, (c) both recycled and virgin polymer layer 0.015 cm, (d) recycled polymer layer 0.02 cm, virgin polymer layer 0.01 cm

Kinetics of contaminant transfer into the food

The kinetics of contaminant transfer into the food are drawn in Fig. 3 for four packagings by plotting M_t/M_{in} vs. $\sqrt{Dt}/L$, where the volume of food is 1.5 cm^2/cm^2 of package.

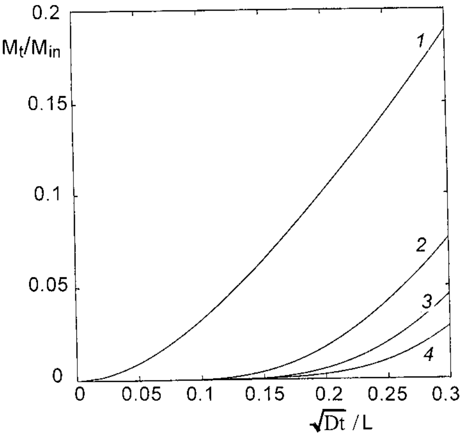


Fig. 3. Kinetics of contaminant transfer (M_t/M_{in}) into food for the four packages (thickness of the recycled polymer layer given): *1* 0.03 cm, 2 0.02 cm, *3* 0.015 cm, *4* 0.01 cm.

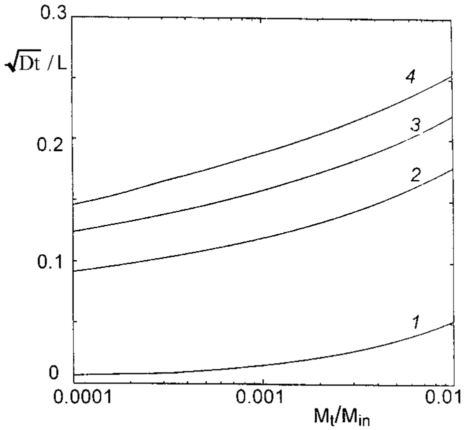


Fig. 4. Time necessary for a given transfer of contaminant (M_t/M_{in}) to take place. For the denotion of curves, see Fig. 3.

Some conclusions from these curves are worth noting:

(i) The slopes of these kinetic curves at the beginning of the process are very low. This is due to the finite value of the coefficient of convective transfer *h*.

(ii) Clearly, the transfer of contaminant into the food starts from the beginning when there is no functional barrier (curve 1). The presence of a functional barrier is responsible for a period of time over which the food is protected from contamination.

(iii) The following statement holds for the kinetics of release: the larger the thickness of the functional barrier, the slower the kinetics of transfer.

The time necessary for a given transfer of contaminant into the food is evaluated in Fig. 4 by plotting the time or, rather, the dimensionless number $\sqrt{Dt}/L$ as a function of the ratio M_t/M_{in} (logarithmic scale) for the four packages. The effect of the functional barrier clearly appears: the presence of a functional barrier increases the time necessary for given transports; this time increases with the thickness of the functional barrier.

Effect of the volume of the food

The effect of the volume of the food on the kinetics of contaminant transfer is shown in Fig. 5 and the time dependence of the contaminant concentration in the food in Fig. 6. In both figures, the dimensionless number $\sqrt{Dt}/L$ is used instead of time. Three values of the volume of food per unit area of package are considered and the corresponding volumes of food are given. For all these volumes, the package with equal thickness (0.015 cm) for each polymer layer is considered.

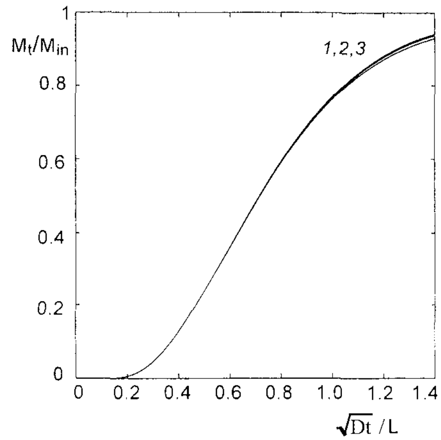


Fig. 5. Amount of contaminant transfer into food vs. (time)$^{0.5}$ for various food volumes: *1* 216 cm^3 (1cm^3/cm^2); *2* 729 cm^3 (1.5 cm^3/cm^2); *3* 1728 cm^3 (2 cm^3/cm^2). (Both recycled and virgin polymer 0.015 cm.)

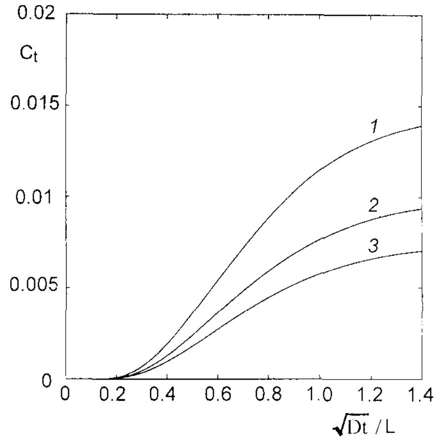


Fig. 6. Relative concentration of contaminant in the food (C_t/C_{in}) as a function of time) for various volumes of food. (For other details, see Fig. 5.)

The following conclusions are of interest:

(i) The kinetics of transfer are the same from the beginning of the process up to around M_t/M_{in} = 0.5, considering the amount of contaminant transferred (Fig. 5). A very slight difference thus appears developing slowly for longer times of contact: the amount of contaminant in the food in equilibrium increases with the volume of food, as shown in Eq. 12:

$$C_{in} \,.\, L_1 = C_{eq} \,.\, L_2 + C_{eq} \,.\, (L - L_2) \qquad (12)$$

(ii) The concentration of contaminant in the food largely depends on the volume of the food in an obvious way: the larger the volume of the food, the lower the concentration of contaminant.

(iii) The period of time over which the food is protected from contamination only depends on the characteristics of the package, and not on the volume of the food.

CONCLUSIONS

The use of a numerical model is of a great help for determining the kinetics of contaminant transfer in the food as well as the concentration profiles of contaminant developed through the package. The role of two main parameters, relative thickness of the recycled and virgin polymer layers in the package and the volume of the food, has been investigated.

Some conclusions are of interest for each case. The functional barrier clearly has two advantages: it is responsible for a period of time over which the food is protected from contamination and the rate of pollution of the food is very low after this time of protection, increasing very slowly. The profiles of concentration of contaminant developed through the package give a fuller insight into the nature of the process.

The volume of the food is also of interest and two results are worth noting: the period of time over which the food is protected only depends on the characteristics of the package and considerably on the thickness of the functional barrier. The kinetics of contaminant transfer in the food are similar, whatever the volume of food, if the ratio M_t/M_{in} is lower than 0.5, the concentration of contaminant being obviously larger if the volume is smaller.

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