

Kinetics of Diffusion of a Pollutant from a Recycled Polymer Through a Functional Barrier: Recycling Plastics for Food Packaging

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Received 14 August 1996; accepted 1 February 1997

ABSTRACT: Recycled polymers containing a pollutant can be used for food packaging if the food is protected by a functional barrier made of virgin polymer. The mathematical treatment of the diffusion of pollutant through the packaging is established when the diffusivity is constant and when there is no transfer through the packaging–food interface. A functional barrier not only reduces but also delays migration during a lag phase. An increase in the relative thickness of the functional barrier dramatically increases its efficiency. Practical examples are presented. The difficulties of control of migration through functional barriers are pointed out. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 597–607, 1997

Key words: recycling; food packaging; functional barrier; food safety; plastics

INTRODUCTION

Recycling of packaging plastics to produce new food packages can be achieved efficiently if the collection, control, and processing of wasted materials can be mastered. The main difficulty is that wasted packages might have come into contact with substances other than food, which may not be harmless. In the new life of the package, these substances may migrate from the recycled packaging material into the food. The Food and Drug Administration (FDA) has proposed definitions and practical means with this purpose in mind.¹ One of the most interesting approaches consists in reusing the wasted plastic as the core of the new material, a layer of virgin polymer being placed between the recycled material and the

food. The FDA calls this virgin polymer a functional barrier.

In the original definition, it was suggested that a functional barrier reduced the migration to a level that could be acceptable from the toxicological point of view. Toxicologists were therefore asked to give advice about acceptable daily intakes of pollutants whose identities were not known. Based on toxicity data of hundreds of known chemicals, the FDA evaluated the risk linked to the ingestion of an unknown chemical.² They considered that a migration of 10 ppb in food represented an acceptable risk.³

In line with this approach, Begley and Hollifield calculated that the thickness of a poly(ethylene terephthalate) functional barrier had to be at least 25 μm thick in order to ensure that migration into food would not exceed 10 $\mu\text{g}/\text{kg}$.⁴ They considered two approaches: one for monolayer and one for bilayer materials. In the first case, the polymer was assumed to be a semi-infinite me-

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dium with a constant concentration of pollutant, while the concentration in the food was constantly zero. The amount of pollutant transferred was proportional to its concentration in the polymer and to the square root of time. In the second case, with a two-layer package, the functional barrier isolating the recycled polymer layer from the food was assumed to play the role of a membrane with constant concentrations on both sides, namely in the food and in the recycled layer. The amount of pollutant entering the food was thus given in terms of a series. In spite of the fact that these two approaches do not correspond to the bilayer problem with diffusion through the two layers and transfer into the food, the idea that diffusion through a functional barrier can be modelled emerges with great interest. This suggests that a predictive model might replace or complement the toxicological approach in some cases.

The whole problem of diffusion in polymers in contact with liquid food is very complex from a theoretical point of view.^{5,6} Various parameters may affect the efficacy of the functional barrier, such as the nature of the polymer and of the pollutants, as well as their mutual compatibility; the transfer of the food into the polymer, which may enhance the diffusivity of the pollutants⁷; the nature of the food; and the level of the pollutant in the recycled layer and the thickness of each polymer layer.

In order to find a solution for these highly complex problems of diffusion, the best way consists in dividing the whole process into its various stages, then considering each stage successively, while keeping in mind that they should be considered simultaneously later. Prior to any experimental work, there is a need for theoretical investigation for predicting the behavior of various materials.

We have undertaken a theoretical study in order to determine the influence of the nature of some pollutants and polymers and to evaluate the effect of the thicknesses of the polymer layers on the diffusion time of these pollutants through the polymers. The first purpose in this study is to consider the Fickian diffusion of the contaminant through the polymer layers and to establish analytical solutions of the problem through mathematical processing. Only the transfer of the pollutant is considered, while its diffusivity is considered to be constant. The packaging consists of two polymer layers: one made of the recycled polymer and the other one being the functional barrier. The second objective of this article is to determine relevant data, such as concentration profiles of

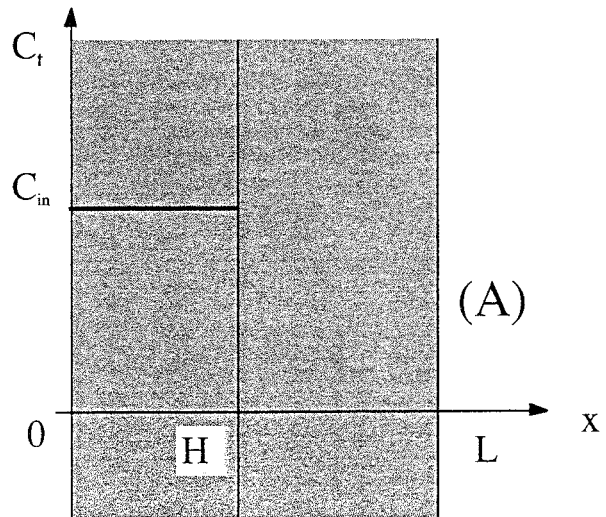


Figure 1 Scheme of the two layer packaging at $t = 0$, with the recycled film of thickness H and the functional barrier of thickness $L - H$: (A) surface intended to come in contact with food.

the pollutant developed through the packaging; the concentration-time history of the pollutant on the surface, which is intended to be in contact with the food; and the time necessary for the pollutant to reach given levels on this surface. Calculations are made for various liquid-polymer couples by using published diffusion constants.

THEORETICAL

As the whole problem of diffusion in polymer packaging is highly complex, a simplified, but still very practical problem is considered in this article. This is precisely defined by the following basic assumptions.⁸

Assumptions

- (1) The packaging consists of two layers of the same polymer in perfect contact (Fig. 1). There is no resistance to mass transfer at the interface between the two layers. This assumption is quite reasonable, as the two polymer layers are not stuck, but melted together by coextrusion.
- (2) We consider the behavior of a single contaminant. Initially, its concentration is uniform in the recycled layer, while the functional barrier is free from contaminant. In other words, the profile of concen-

tration of the contaminants is supposed to be vertical at the polymer layers interface. This is surely questionable. However, for the time being, it is very difficult and not yet done to determine this profile of concentration. If the real concentration profile of the pollutant was known, it would be possible to treat the problem by using a numerical model.

- (3) The transfer of contaminant is controlled by Fickian diffusion, the polymers being in the elastomeric state.
- (4) The diffusivity of the contaminant is constant and identical in both polymer layers. This is not too far from reality since the two layers are made from the same polymer. The transport is unidirectional.
- (5) There is no transfer of contaminant through the two external surfaces of the packaging. In reality, some losses may occur, especially if the pollutant is volatile. However, we will focus on an initial period of storage, where such losses by vaporization are reduced. In any case, the rate of evaporation is expected to be low.
- (6) No food enters the polymer. We are considering here the evolution of a package before it comes into contact with food.
- (7) The thickness of each layer remains constant. Swelling of the polymer is considered negligible since the concentration of the pollutant is expected to be very low.

Mathematical Treatment

The equation for unidirectional diffusion with a constant diffusivity (assumption 4) is

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

where $C_{x,t}$ is the concentration of contaminant at position x and time t , and D is the constant diffusivity of the pollutant.

The initial and the boundary conditions shown in assumptions 2, 1, and 5, respectively, are expressed by

$$t = 0 \quad 0 < x < H \quad C = C_{in} \quad (2)$$

$$H < x < L \quad C = 0 \quad (2a)$$

$$t > 0 \quad \left(\frac{\partial C}{\partial x} \right)_{x=0} = \left(\frac{\partial C}{\partial x} \right)_{x=L} = 0 \quad (3)$$

H and L are the thicknesses of the recycled layer and of the whole material, respectively (Fig. 1). C_{in} is the initial concentration of the pollutant in the recycled polymer.

Following assumptions 3, 4, and 6, mathematical processing is feasible.^{5,9} In this case, the analytical solution is obtained using the method of separation of variables.

The concentration of pollutant $C_{x,t}$ is thus expressed as a function of time by eq. (4), as follows:

$$\frac{C_{x,t}}{C_{in}} = \frac{H}{L} + \frac{2}{\pi} \cdot \sum_{n=1}^{\infty} \frac{1}{n} \cdot \sin \frac{n\pi H}{L} \cdot \cos \frac{n\pi x}{L} \times \exp\left(-\frac{n^2\pi^2}{L^2} Dt\right) \quad (4)$$

The concentration of pollutant on the surface of the packaging in contact with the food is obtained by putting $x = L$ in eq. (4), as follows:

$$\frac{C_{L,t}}{C_{in}} = \frac{H}{L} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi H}{L} \times \exp\left(-\frac{n^2\pi^2}{L^2} Dt\right) \quad (5)$$

When the ratio of the thicknesses H/L is very small, eq. (5) reduces to

$$\frac{C_{L,t}}{C_{in}} = \frac{H}{L} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \cdot \exp\left(-\frac{n^2\pi^2}{L^2} Dt\right) \right] \quad (5a)$$

and, for long times, the first term of the series in eq. (5a) becomes preponderant, leading to

$$\frac{C_{L,t}}{C_{in}} = \frac{H}{L} \left[1 - 2 \cdot \exp\left(-\frac{\pi^2}{L^2} Dt\right) \right] \quad (5b)$$

The amount M_t of contaminant transferred into the functional barrier at time t is obtained by integrating the concentration $C_{x,t}$ with respect to space between the abscissae H and L . M_t is expressed as a fraction in eq. (6) of the amount M_{in} of contaminant initially located in the recycled layer.

$$\frac{M_t}{M_{in}} = \frac{L - H}{L} - \frac{2L}{\pi^2 \cdot H} \cdot \sum_{n=1}^{\infty} \frac{1}{n^2} \left(\sin \frac{n\pi H}{L} \right)^2 \times \exp\left(-\frac{n^2 \pi^2}{L^2} Dt\right) \quad (6)$$

All the equations are expressed in terms of the dimensionless numbers $\frac{Dt}{L^2}$ for the time, $\frac{H}{L}$ for the relative thickness of the barrier, $\frac{M_t}{M_{in}}$ for the amount of pollutant transferred, and $\frac{C_{x,t}}{C_{in}}$ for the concentration of pollutant.

RESULTS

Three kinds of results are of interest: the concentration profiles of the contaminant developed through the packaging; the concentration-time history of the contaminant at the surface in contact with the food; the kinetics of mass transfer of the contaminant.

In order to get general results that can be of use in all practical situations corresponding to the

basic assumptions 1-7, we have calculated master curves using the dimensionless numbers $\frac{Dt}{L^2}$,

$$\frac{H}{L}, \frac{M_t}{M_{in}}, \text{ and } \frac{C_{x,t}}{C_{in}}.$$

Profiles of Concentration of Contaminant

The concentration profiles calculated using eq. (4) are drawn in Figures 2-4 for various values of the thicknesses ratio H/L ranging from 1/2 to 1/4.

The following conclusions can be drawn.

- (1) At the very beginning ($\frac{Dt}{L^2} \leq 0.004$), the concentration of contaminant falls abruptly at the interface of the two polymer layers down to $C_{in}/2$: $\frac{C_{H,t}}{C_{in}} = \frac{1}{2}$.
- (2) For values of Dt/L^2 lower than 0.004, the profiles in the two layers are symmetrical, with the point of symmetry being at the interface, with $C_{H,t}/C_{in} = 1/2$. This is true, whatever the thicknesses of the layers.
- (3) The effect of the thickness of the functional barrier appears for $Dt/L^2 \geq 0.004$. The

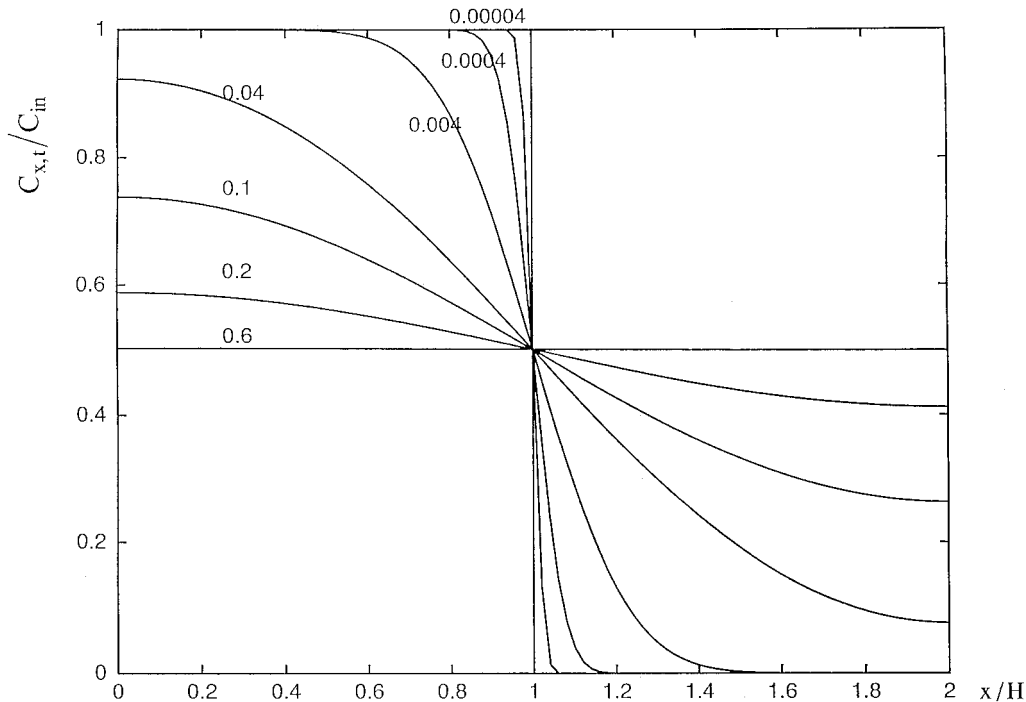


Figure 2 Profiles of concentration of contaminant developed through the packaging with the ratio $H/L = 1/2$ for various times (values of Dt/L^2 are shown).

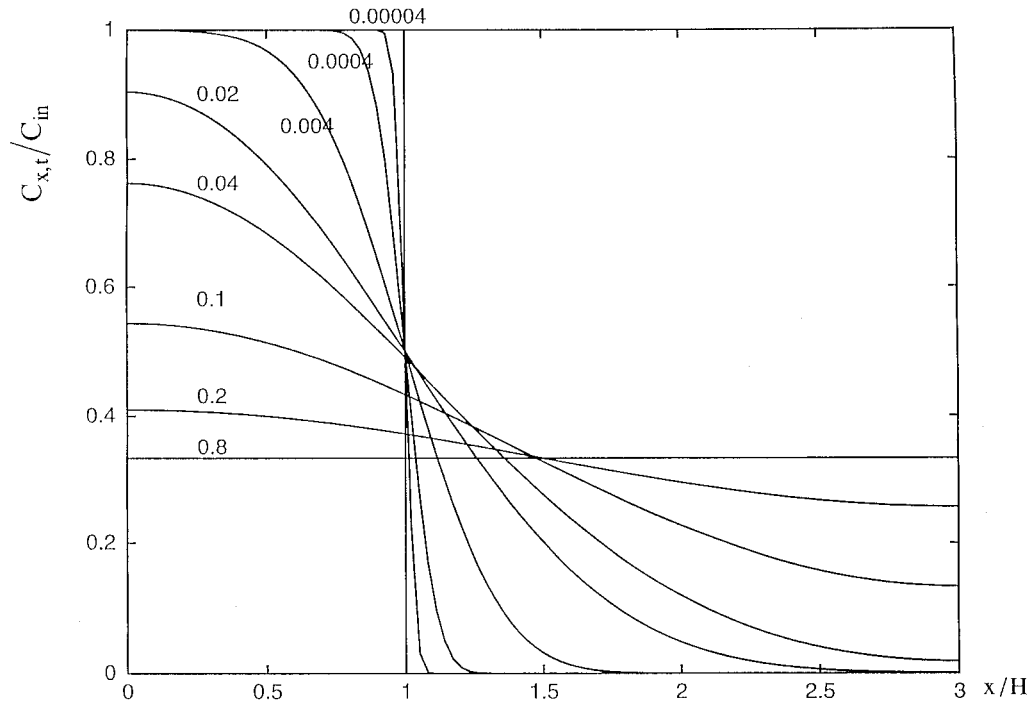


Figure 3 Profiles of concentration of contaminant developed through the packaging with the ratio $H/L = 1/3$ for various times (values of Dt/L^2 are shown).

curves remain symmetrical only when the two layers have the same thickness ($H/L = 1/2$; Fig. 2).

- (4) At equilibrium after infinite time, the trigonometrical series tend towards zero, and the uniform contaminant concentration throughout the packaging is given by the simple relation, $C_{x,\infty}/C_{in} = H/L$. In fact, for a value of Dt/L^2 around 0.8, equilibrium is nearly reached (Figs. 2–4).
- (5) The gradient of concentration is flat on the two external surfaces of the packaging, at $x = 0$ and $x = L$, since there is no mass transport through these surfaces, following the boundary conditions [eq. (3)].

Concentration $C_{L,t}$ of Contaminant on the Surface of the Packaging That is to Come in Contact with Food

It is essential to have good knowledge of the concentration–time history of the contaminant on the packaging surface that is to be in contact with the food. The increase in concentration with time as a function of Dt/L^2 is drawn in Figure 5 for various values of the ratio of the thickness of the two layers H/L .

Important conclusions can be drawn.

- (1) Initially, the virgin polymer layer plays the role of a highly efficient functional barrier, as shown in Figure 5. No mass transport appears on this surface up to a given time. This corresponds to a lag time behavior.
- (2) After this time, the concentration of contaminant increases with time, as shown more precisely in Table I, where the ratio $C_{L,t}/C_{in}$ is evaluated at various values of Dt/L^2 and for different thicknesses H/L .
- (3) The master curves drawn in Figure 5, as well as the values shown in Table I, can be used in all typical cases.
- (4) The effect of the relative thicknesses of the two polymer layers, especially at initial stages, is well illustrated in Figure 6, where $L_n(C_{L,L}/C_{in})$ is plotted against H/L for various values of Dt/L^2 .
- (5) The master curves in Figures 5 and 6 can be used for determining the period of highest efficiency of the functional barrier. During this period of high efficiency, the contaminant concentration on the surface ($x = L$) is very low. Table II illustrates how the mathematical equations can be applied to predict the lag phase in practical situations. Calculations are made for the following three typical low-molecular-weight,

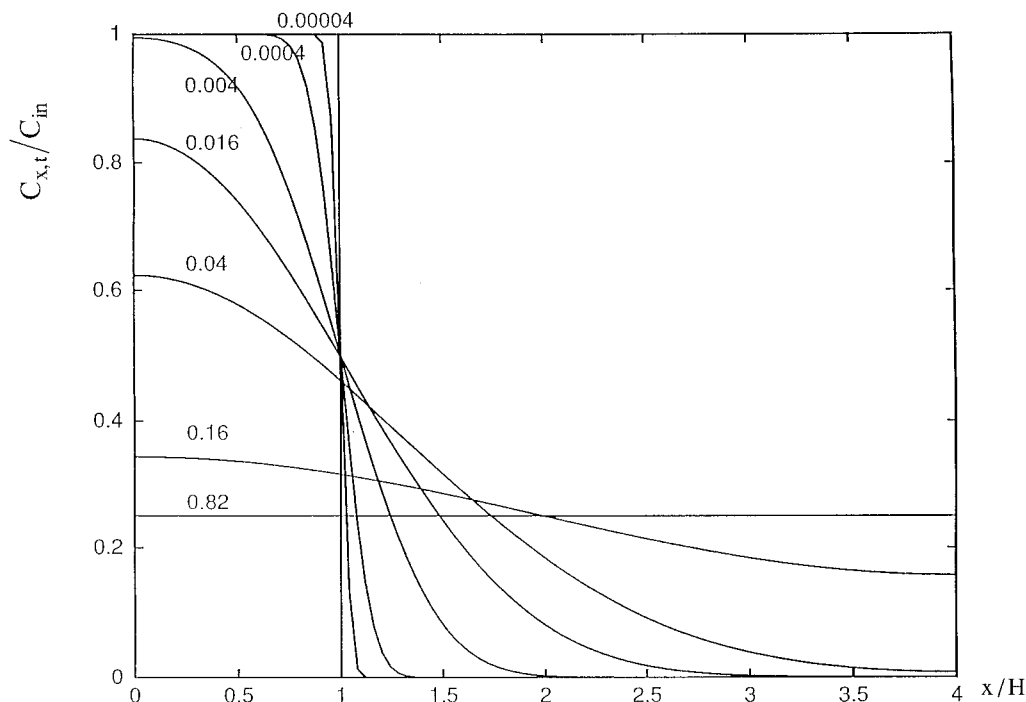


Figure 4 Profiles of concentration of contaminant developed through the packaging with the ratio $H/L = 1/4$ for various times (values of Dt/L^2 are shown).

fast-diffusing pollutants: limonene, ethyl acetate, and trichloroethylene, and for a given thickness of the recycled layer (50 μm). The polymer-pollutant couples are characterized by the diffusivity D of the pollutant in the polymer. For instance, when the two layers have the same thickness ($H/L = 1/2$), Table I shows that the concentration on the surface ($x = L$) reaches 1.2% of the initial concentration ($C_{L,t}/C_{in} = 0.012$) when $Dt/L^2 = 0.02$. For limonene in polypropylene ($D = 0.65 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$),¹⁰ the corresponding time is 3.1 days. The times necessary for the ratio of concentrations on the surface $C_{L,t}/C_{in}$ to reach values of 0.001 and 0.01 are shown in Table II for the three contaminant-polymer couples, using diffusivities taken from literature.

- (6) In fact, from the dimensionless number Dt/L^2 , the time necessary for a given transport is inversely proportional to the diffusivity, as shown in eq. (4). Thus, the values of the times in the second and third contaminant-polymer couple can be easily extrapolated from the times shown for the first contaminant-polymer couple. The ratio of the thicknesses of the two polymer

layers appears in eqs. (4) and (5), as well as the thickness of the packaging L in the dimensionless number Dt/L^2 . Thus, the time necessary to reach a given transport is not proportional to the thickness L of the packaging but strongly increases with H/L .

Kinetics of the Contaminant Transfer Through the Two Polymer Layers

The kinetics of contaminant transfer from the recycled layer into the functional barrier is calculated using eq. (6). They are drawn for various values of the thicknesses H/L in Fig. 7 for long times (or rather Dt/L^2).

These results solicit the following comments.

- (1) A vertical tangent is observed at the beginning of the process, corresponding to a very high rate of contaminant transfer. This situation results from the perfect contact between the two polymer layers at abscissa H .
- (2) The rate of mass transfer decreases exponentially with time or with the dimensionless number Dt/L^2 .
- (3) The end of the process, from the theoretical point of view, is attained after infinite time. From a practical point of view, the

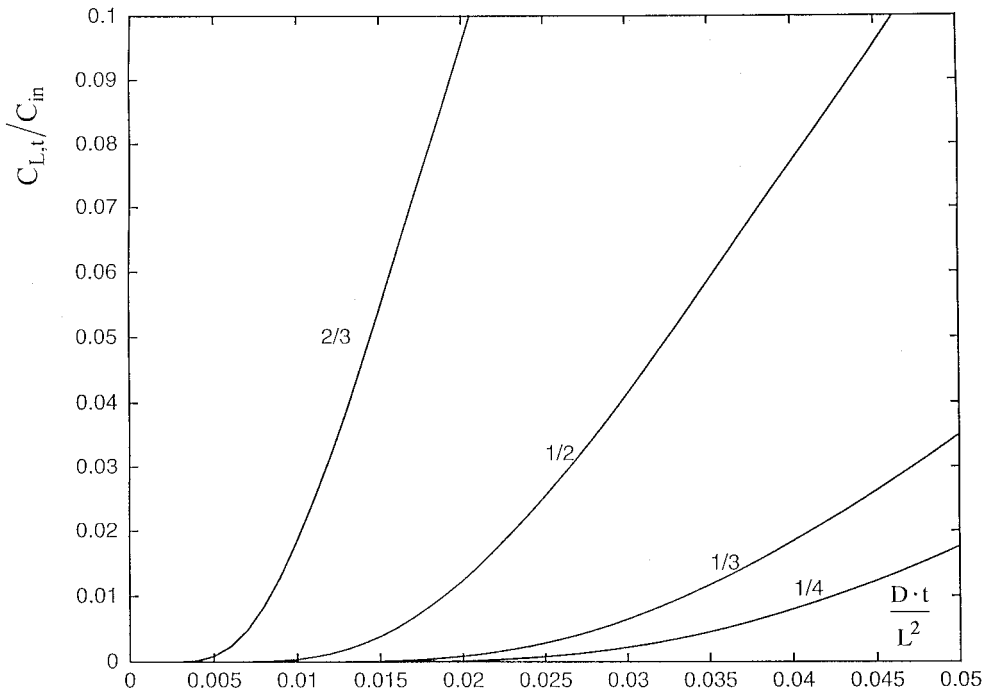


Figure 5 Concentration of contaminant ($C_{L,t}/C_{in}$) on the surface intended to come in contact with food as a function of time (Dt/L^2), with various values of the ratio H/L .

rate of transfer is very low when the dimensionless number Dt/L^2 is 0.8. In Table II, we have calculated the times necessary to reach values of $\frac{C_{L,t}}{C_{\infty}}$ equal to 0.9 and 0.99 for the three pollutant–polymer couples.

DISCUSSION

Properties of a Functional Barrier

This work shows how a functional barrier works. Initially, the concentration $C_{L,t}$ of the pollutant on the surface ($x = L$, Fig. 1) is very low and can be assimilated to zero. During this period, the

pollutant diffuses through the functional barrier. When it reaches the surface meant to come into contact with food ($x = L$) in the package, $C_{L,t}$ slowly increases. This behavior is typical of lag time behavior. For longer times, the pollutant is diluted over the two layers, thus reducing migration. A legal definition of the functional barrier should therefore specify that it both delays and reduces migration. During the lag phase, no contaminant reaches the surface meant to come in contact with food. If there was contact with food, then no migration could occur during the lag phase. This is a first remarkable property of materials having a functional barrier.

The introduction of the lag phase concept in the definition of functional barriers has important

Table I $C_{L,t}/C_{in}$ at the External Surfaces Versus Time (Dt/L^2) for Various Relative Thicknesses H/L

H/L	$Dt/L^2 \times 100$						
	0.1	0.2	0.5	1	1.5	2	2.5
2/3	$< 10^{-7}$	1.4×10^{-7}	8.6×10^{-4}	1.8×10^{-2}	5.4×10^{-2}	9.5×10^{-2}	17×10^{-2}
1/2	$< 10^{-7}$	$< 10^{-7}$	5.7×10^{-7}	4.1×10^{-4}	3.9×10^{-3}	1.2×10^{-2}	4.1×10^{-2}
1/3	$< 10^{-7}$	$< 10^{-7}$	$< 10^{-7}$	2.4×10^{-6}	1.2×10^{-4}	8.6×10^{-4}	6.5×10^{-3}
1/4	$< 10^{-7}$	$< 10^{-7}$	$< 10^{-7}$	1.1×10^{-7}	1.5×10^{-5}	1.8×10^{-4}	2.2×10^{-3}

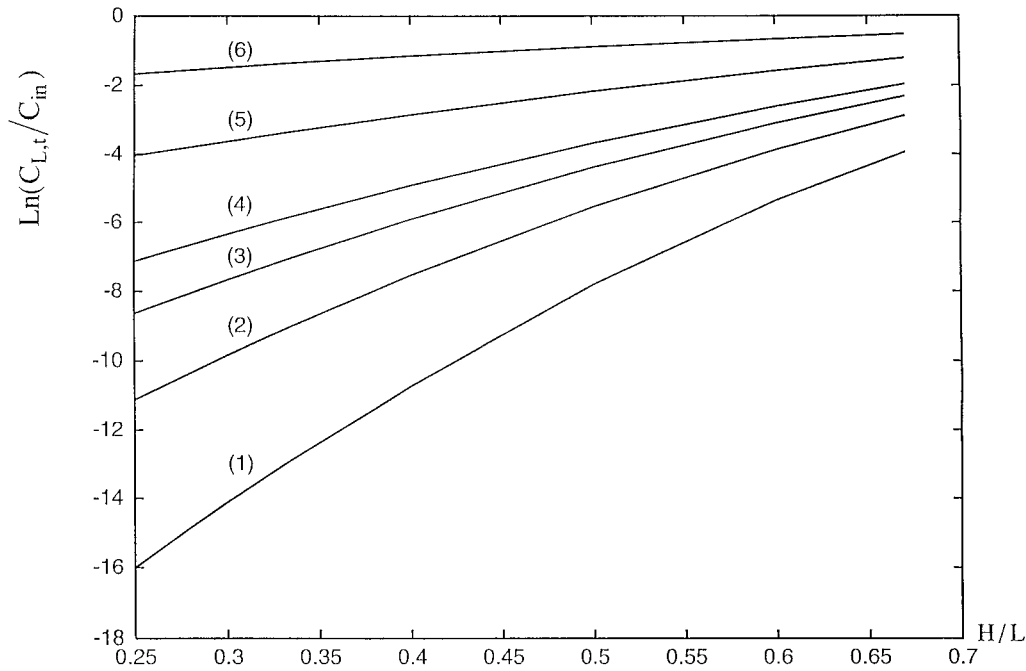


Figure 6 Concentration of contaminant on the surface [$\ln(C_{L,t}/C_{in})$] as a function of the ratio H/L for various values of Dt/L^2 : (1) $Dt/L^2 = 0.01$; (2) $Dt/L^2 = 0.015$; (3) $Dt/L^2 = 0.02$; (4) $Dt/L^2 = 0.025$; (5) $Dt/L^2 = 0.05$; (6) $Dt/L^2 = 0.2$.

practical consequences. If it can be demonstrated that the use of the package occurs during the lag phase, no migration can occur; and there is no toxicological concern, and no need to estimate an

acceptable risk linked to a contamination of food by the pollutant. This allows the shifting of a difficult control of migration to a control of the source of recycled polymer and of the process.¹¹

Table II Time (Days) Associated With Given Concentrations $C_{L,t}/C_{in}$ or $C_{L,t}/C_z$ on the Surface with $H = 50 \mu\text{m}$

Thickness (L_p in μm)	$C_{L,t}/C_{in}$	$C_{L,t}/C_z$	Limonene/PP ^a ($D = 0.65 \cdot 10^{15} \text{ m}^2\text{s}^{-1}$)	Ethyl acetate/PP ^a ($D = 15 \cdot 10^{15} \text{ m}^2\text{s}^{-1}$)	Trichloroethylene/HDPE ^b ($D = 520 \cdot 10^{15} \text{ m}^2\text{s}^{-1}$)
100	0.001 ^c	—	2.06	0.089	0.0026
100	0.01 ^c	—	3.35	0.14	0.0042
100	—	0.9 ^d	45.90	1.99	0.058
100	—	0.99 ^d	87.44	3.79	0.11
200	0.001 ^c	—	18.52	0.80	0.023
200	0.01 ^c	—	30.1	1.31	0.038
200	—	0.9 ^d	208.6	9.04	0.262
200	—	0.99 ^d	374.8	16.24	0.469
500	0.001 ^c	—	168.3	7.2	0.210
500	0.01 ^c	—	286.9	12.43	0.359
500	—	0.9 ^d	1343.7	58.22	1.68
500	—	0.99 ^d	2382.3	103.23	2.98

^a See Franz¹⁰.

^b Prasad et al.¹⁷.

^c Describing the lag phase.

^d Describing how the system reaches equilibrium; PP = polypropylene; HDPE = high-density polyethylene.

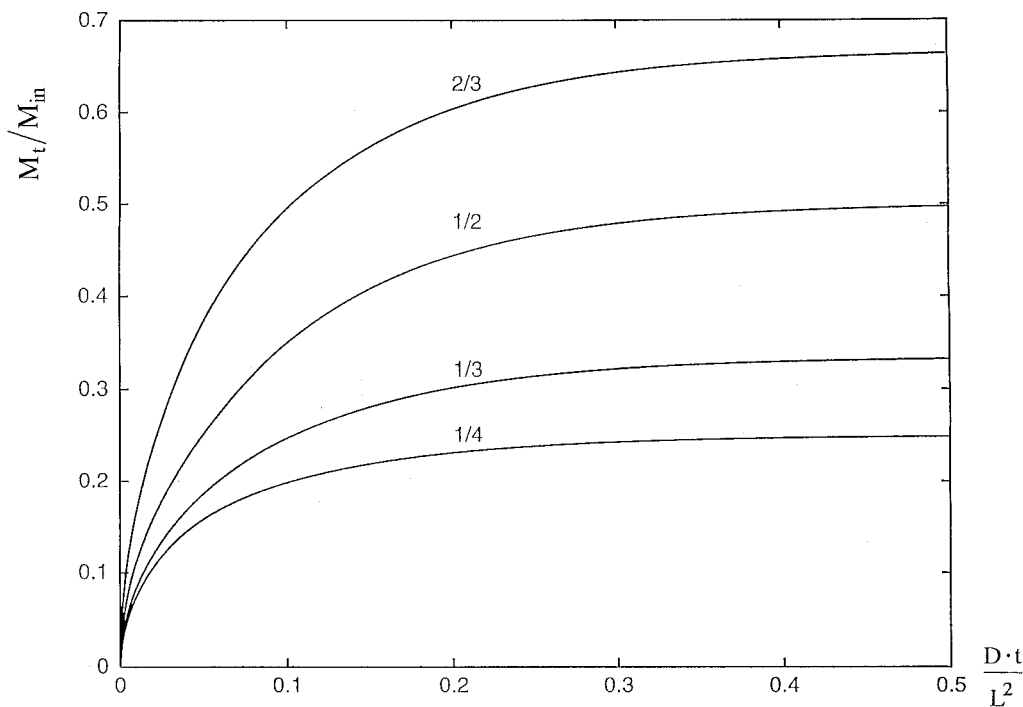


Figure 7 Kinetics of contaminant transfer within the two layer packaging for various values of the thicknesses of the polymer layers H/L .

Testing Migration Through Functional Barriers

The diffusion kinetics of the pollutant (Fig. 6) have a consequence on official methods to control migration. With monolayer materials, when the viscosity of the food is low and when the migrant dissolves readily in food, migration increases linearly with the square root of time of contact in an initial period.⁵ Then, migration at $t = 360$ days cannot exceed six times the migration occurring at $t = 10$ days. Testing for 10 days, as in official EU procedures, thus gives an overview of the migration over the whole life of the package. The situation is different for multilayer materials like those shown in Figure 1, especially if the functional barrier is efficient. If the lag time is higher than 10 days, no migration will be detected at $t = 10$ d, while migration may become significant for longer test times. If migration had to be determined experimentally, then testing should be carried out over much longer periods, possibly over the whole shelf life, which is not realistic. Furthermore, it must be taken into account that migration starts when the material is manufactured and not when the package is filled, as with monolayer materials. For these reasons, monitoring migration from multilayer materials into food simulants cannot be a general routine method for quality control. A

practical procedure for testing functional barriers has been described,¹²⁻¹⁴ but it is of no practical use, since the kinetic specificities of multilayer materials have been overlooked.

The situation is not easier with alternative control methods. For monolayer materials, practical methods developed to avoid carrying out migration testing according to official procedures were developed; they rely on extraction of the material,^{12,15-16} followed by quantitative and qualitative analysis of the potential migrants. This cannot be used for testing the efficiency of a functional barrier since pollutants from the recycled layer will be present in extracts. If these substances do not belong to a positive list, the material may still be suitable for food contact as long as an unacceptable migration of the pollutants does not occur.

Given all these difficulties, a theoretical approach with calculated kinetic curves should play a major role for the decision to accept a recycled material on the market. The main information needed to predict a worst case situation is the identity of the polymer constituting the functional barrier. This is routinely obtained by microscopic observation associated with infrared spectroscopy. Once the polymer is known, diffusion con-

stants of worst case volatile pollutants can be found in literature.^{12,17} Given the thicknesses of the layers, which can also be determined by microscopy, it is possible to predict the state of the system at any time using the master curves shown here. Before deciding whether a material is suitable for food contact, the influence of elevated temperatures reached during the processing of plastics must be considered: it may induce preferential losses of the most volatile pollutants by vaporization, which renders the material safer; but it may also stimulate the diffusion of the pollutants into the functional barrier.

Definition of the Lag Time

Before lag time, the pollutant diffuses through the barrier without reaching the surface meant to come in contact with food. After lag time, it may migrate into food. The concept of lag time, which is easy to understand with common sense, is difficult to define from a theoretical point of view since the concentration on the surface ($x = L$) can always be calculated, even if it reaches very low values (see Table I; values of $C_{L,t}/C_{in}$ lower than 10^{-7}). Therefore, conventional definitions of lag time are proposed here.

There are two ways to define lag time from a practical point of view. The first possibility consists in saying that lag time is the time necessary to reach $C_{L,t}/C_{in} = 0.001$ ($C_{L,t}$ is 0.1% of the initial concentration). For each material, the corresponding time can then be deduced for the appropriate H/L ratio from Figures 6 and 7 and from Table I.

Another possibility is to give a more general, but more conventional, definition. It can be seen in Table I that when $H/L \leq 1/2$ (which covers all practical situations), $C_{L,t}/C_{in} \leq 0.001$ when $Dt/L^2 = 0.01$. Thus, a conventional definition of lag time is

$$t_{lag}^* = 0.01 \frac{L^2}{D}$$

where t_{lag}^* is the conventional lag time when $H/L \leq 1/2$.

Of course t_{lag}^* depends on the polymer, on the pollutant, and on the thicknesses of the layers. However, worst case pollutants are those that have the largest D values, i.e., the lowest molecular weight.¹⁸

Table II shows typical lag time values of low-

molecular-weight compounds in polyolefines. Since the lag phase occurs till $C_{L,t}/C_{in} = 0.001$, it can be seen that a 450 μm PP layer ($L = 500 \mu\text{m}$; $H = 50 \mu\text{m}$) protects the food from migration of limonene during 168.3 days. For ethyl acetate, lag time is only 7.2 days. If information about the behavior of materials and other pollutants is needed, the relevant data can be deduced from those in Table II by proportionality.

Influence of the Thickness of the Layers and Possible Optimization of the Functional Barrier

The practical effect of the thickness of the functional barrier and of H/L appears clearly from examples given in Table II. When $L = 100 \mu\text{m}$, the material is a poor functional barrier. However, when the relative thickness of the functional barrier increases, $t_{0,001}$ increases strongly with L/H .

This suggests that efficient polyolefine functional barriers can be made in thick materials rather than in films.

After the lag phase, the concentration of the pollutant in the recycled layer increases slowly with time. Gradually, the concentration equilibrates to $C_{in}/2$ (for $L/H = 2$). This is equivalent to a dilution of the pollutant throughout the whole material, which is expected to lead to a reduction of migration, as in the FDA definition. The functional barrier thus behaves as a filter reducing migration. If the material is stored without contact with food, equilibration occurs after long periods of time (see $C_{L,t}/C_{\infty} = 0.9$ and 0.99 in Table II).

The following effect of the thickness of the layers thus appears to be very important for the optimization of a recycled material: lag time strongly increases when the ratio $\frac{H}{L}$ decreases (Fig. 6);

after long periods of time, the smaller the ratio $\frac{H}{L}$, the larger the dilution of the pollutant. Limitations of the present approach mainly concern the kind of polymer; the model does not apply to glassy polymers. However, obviously, they should also exhibit a similar lag phase behavior.

Other approaches have been used to predict the behavior of functional barriers.^{4,12-14} However, they are based on a mathematical model called infinite packaging,¹⁹ which does not take into account the possible diffusion of the pollutant in the recycled layer, nor the influence of the thickness.

CONCLUSIONS

As shown in this article, the functional barrier acts on the transfer of contaminant from the recycled polymer layer in two ways. First, it retards the migration of the contaminant into the food as it takes some time for the contaminant to diffuse through the virgin layer. In that sense, this layer plays the role of a functional barrier. Secondly, the contaminant tends to be uniformly distributed through the bilayer packaging after long periods of time. Thus, a dilution of the contaminant occurs during the process. Obviously, the final concentration of contaminant depends on the thicknesses of the two polymer layers.

Another result of interest appears with the concentration–time history of contaminant on the surface of the packaging in contact with the food.

The results are expressed in terms of dimensionless numbers; thus, they are of use in any of the cases corresponding to the basic assumptions taken in this article. The time of protection has been evaluated from these results in typical cases for various thicknesses of the two polymer layers. The results suggested that typical official test conditions defined for monolayer materials cannot be used for the control of a functional barrier. Given the state of the art, only a predictive approach can be of help in deciding whether a functional barrier is efficient and whether recycled plastics, although possibly polluted, can be used safely. During the lag phase, the food is completely protected from migration of the pollutant. After the lag phase, a low migration can be expected. Introducing the concept of lag phase enables to define practical conditions of use of the material. This work also shows how a material can be optimized by playing with the thicknesses of the two layers. For symmetry reasons, the same approach can be used to describe three-layer materials, where the recycled polymer is in the middle. Practical validations of the model should allow to take into account crystallinity effects¹⁸ on functional barrier properties.

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