

# Contaminant transfer during the processing of thick three-layer food packages with a recycled polymer between two virgin polymer layers

Contaminant  
transfer

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## Nomenclature

|           |   |            |  |
|-----------|---|------------|--|
| A         | = constant in the temperature-dependent diffusivity   | $\rho$     | = density of the polymer ( $\text{g}/\text{cm}^3$ )  |
| c         | = heat capacity ( $\text{cal}/\text{g}\cdot\text{deg}$ )  | $P_j^i$    | = Dimensionless number defined in equation (11) at position $j\Delta x$ and time $i\Delta t$ |
| $C_j^i$   | = concentration of contaminant at time $i\Delta t$ and $j\Delta x$  | $M_{in}$   | = Amount of contaminant initially in the recycled layer                                      |
| $C_{x,t}$ | = concentration at position $x$ and time $t$  | $Mt$       | = Amount of contaminant transferred after time $t$   |
| $C_{in}$  | = initial uniform concentration of contaminant in the recycled polymer  | $N_j^i$    | = Dimensionless number defined in equation (14) at position $j\Delta x$ and time $i\Delta t$ |
| $D_j^i$   | = diffusivity of the contaminant at position $j\Delta x$ and time $i\Delta t$   | $T_a, T_m$ | = temperature of air, of the mould, respectively   |
| $D_o$     | = constant in the temperature-dependent diffusivity   | $T_L$      | = temperature on the package surfaces  |
| $\lambda$ | = thermal conductivity  | $t_h$      | = time of heating in the mould   |
| $h_m$     | = coefficient of heat transfer at the mould-polymer interface ( $\text{cal}/\text{cm}^2\cdot\text{s}\cdot\text{deg}$ )          | $U_L^i$    | = Dimensionless number defined in equation (11) at the surface and time $i\Delta t$          |
| $h_a$     | = coefficient of convective heat transfer at the polymer-air interface ( $\text{cal}/\text{cm}^2\cdot\text{s}\cdot\text{deg}$ ) | $x$        | = abscissa   |
| L         | = thickness of the sheet (cm)   | $x/L$      | = relative abscissa used in figures for profiles of temperature and of concentration         |

## Introduction

Amongst the ways of recycling old polymers[1], one of them consists of reusing old food packages as new food packages[2-4]. During its first use as food packages, the polymer is generally contaminated, the food or other materials diffusing into the polymer[5-9]. In order to prevent food from potent contamination by the recycled polymer, bi-layer or tri-layer packages are prepared, a virgin polymer layer being located between the recycled polymer and the food. The contaminant is transferred by diffusion through the polymer layers[10,11] and either by convection into the liquid food[12] or by diffusion through the solid food[13,14]. As it takes some time for the contaminant to diffuse through the package, the virgin polymer plays the role of a functional barrier and the problem which arises is to predict the period of time over which the food is protected. The mathematical treatment of diffusion through the polymer package alone is feasible when the diffusivity is constant[10,11]. In the

common case when the package of finite thickness is in contact with a food of finite volume with a finite coefficient of convection transfer, only a numerical treatment of the problem is feasible[12,13], in spite of an attempt of mixing two analytical solutions obtained either with a finite volume of food and infinite coefficient of convection transfer or with an infinite volume of food and finite coefficient of transfer[15]. The present studies are made with two main assumptions: the one is concerned with the food transfer into the polymer which is neglected, in spite of the fact that it often intervenes by enhancing the contaminant transfer in the food[16,17]; the other with the uniform concentration of the contaminant in the recycled polymer layer, while the new polymer layers are free from contaminant.

The first objective of this paper is to look upon the validity of the second assumption, by considering deeply the process of heat transfer and mass transfer during the processing of the packages. Three thick polymer layers are selected either with the same thicknesses or with different thicknesses, and the contaminated polymer layer is located between two virgin polymer layers. Being prepared by pressing the layers in a heated mould, the processing is controlled by heat transfer by conduction through the polymer layers with a high coefficient of heat transfer at the mould-package interface and by heat conduction and free convection after extraction of the package out of the mould during the cooling period in air. The process with this type of three-layer package is different from that developed in a bi-layer package as no evaporation of the contaminant takes place during the processing[18]. In the same manner, the process is more complex in thermoforming thick layers than in coextrusion of thin layers[19].

The other purpose in this study is to build a numerical model taking into account all the known facts during the processing concerning either heat transfer or mass transfer: heat transfer by conduction through the heating period in the mould kept at constant temperature with a high coefficient of heat transfer at the polymer-mould interface, and during the cooling period after removal of the package from the mould heat transfer by conduction through the polymer with a free convection at the polymer-air interface. The contaminant transfer takes place either during the heating period in the mould or the cooling period, when the temperature is high, this transfer being controlled by transient diffusion with a temperature-dependent diffusivity. Two types of packages are considered: the one with the same thickness for each layer, the other with layers of different thicknesses. The results are expressed in terms of master curves by using dimensionless numbers as much as possible.

### **Theoretical**

#### *Assumptions*

In order to clarify the process the following assumptions are made :

- The package is made of three polymer layers, a recycled polymer being located between two virgin polymer layers.

- Initially, the contaminant concentration is uniform in the recycled layer, while the other two layers are free from contaminant.
- The three polymer layers are in perfect contact, with no resistance to heat or mass transfer at their two interfaces.
- The process of heating consists of the following two stages: when the polymer sheets initially at room temperature are pressed into the slabs of a mould kept at constant temperature over a period of time  $t_h$ ; when the package is allowed to cool down in motionless air at room temperature, after extraction from the mould.
- The process of heating is controlled by heat conduction through the thickness of the sheets with a high coefficient of heat transfer at the package-mould interface, and by heat conduction and free heat convection in motionless air.
- During the two stages of heating, the transfer of the contaminant through the polymer is controlled by transient diffusion with a temperature-dependent diffusivity.
- During the cooling period in motionless air, the contaminant does not evaporate from the external surfaces of the packaging.

*Mathematical treatment*

*Heat transfer.* The equation of uni-directional heat transfer through the thickness of the package is:

$$\rho c. \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( \lambda. \frac{\partial T}{\partial x} \right) \quad (1)$$

The initial condition is :

$$t = 0 \quad 0 < x < L \quad T = T_{in} \quad (2)$$

and the boundary conditions are:  
in the mould:

$$t < t_h \quad x = 0 \quad - \lambda \frac{\partial T}{\partial x} = h_m (T_L - T_m) \\ \text{and} \quad x = L \quad (3)$$

in motionless air :

$$t > t_h \quad x = 0 \quad - \lambda \frac{\partial T}{\partial x} = h_a (T_L - T_a) \\ x = L \quad (4)$$

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A condition of symmetry exists at the midplane written as follows

$$t > 0 \quad x = \frac{L}{2} \quad \frac{\partial T}{\partial x} = 0 \quad (5)$$

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*Mass transfer.* The equation of uni-directional diffusion is :

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \cdot \frac{\partial C}{\partial x} \right) \quad (6)$$

with the temperature-dependent diffusivity  $D_{x,t}$  which thus varies with position  $x$  and time  $t$ .

The initial conditions are :

$$\begin{array}{lll} t = 0 & \text{recycled layer} & C = C_{in} \\ & \text{virgin layers} & C = 0 \end{array} \quad (7)$$

The boundary conditions are obvious with equation (6) in the three layers. Different conditions could appear in case of evaporation of the contaminant on the surface, but this is not the case in this study.

The diffusivity of the contaminant through the polymer varies with temperature following an Arrhenius law :

$$D_T = D_0 \cdot \exp \left( - \frac{A}{T} \right) \quad (8)$$

where  $A$  and  $D_0$  are two constants, and  $T$  is the temperature in K.

*Numerical analysis*

There is no analytical solution for the problem, which is resolved by using the implicit Crank Nicolson method with finite differences.

The problem is resolved step by step by this method, by calculating the temperature and concentration at each position and time.

The temperature is evaluated within the packaging by :

$$\begin{aligned} -\frac{P_{j+0.5}^{i+1}}{2} T_{j+1}^{i+1} + \left( 1 + \frac{P_{j-0.5}^{i+1}}{2} + \frac{P_{j+0.5}^{i+1}}{2} \right) T_j^{i+1} - \frac{P_{j+0.5}^{i+1}}{2} T_{j+1}^{i+1} = \\ \frac{P_{j+0.5}^j}{2} T_{j+1}^j + \left( 1 - \frac{P_{j-0.5}^j}{2} - \frac{P_{j+0.5}^j}{2} \right) T_j^j + \frac{P_{j+0.5}^j}{2} T_{j-1}^j \end{aligned} \quad (9)$$

and at the surfaces of the polymer :

$$\begin{aligned}
 & -P_{L-0.5}^{i+1} T_{L-1}^{i+1} + (1 + P_{L-0.5}^{i+1} + U_L^{i+1}) T_L^{i+1} = \\
 & P_{L-0.5}^i T_{L-1}^i + (1 - P_{L-0.5}^i - U_L^i) T_L^i + (U_L^i + U_L^{i+1}) T_{sur}
 \end{aligned}
 \tag{10}$$

with the dimensionless numbers:

$$P_j^i = \frac{\lambda_j^i}{\rho c} \cdot \frac{\Delta t}{(\Delta x)^2} \quad U_L^i = \frac{h \cdot \Delta t}{\Delta x} \cdot \frac{1}{\rho c}
 \tag{11}$$

where:

$$\begin{cases}
 h = h_m & \text{and } T_{sur} = T_m & \text{if } t < t_h \\
 h = h_a & \text{and } T_{sur} = T_a & \text{if } t > t_h
 \end{cases}
 \tag{11a}$$

The concentration of the contaminant is obtained within the package by:

$$\begin{aligned}
 & -\frac{N_{j+0.5}^{i+1}}{2} C_{j+1}^{i+1} + \left( 1 + \frac{N_{j+0.5}^{i+1}}{2} + \frac{N_{j-0.5}^{i+1}}{2} \right) C_j^{i+1} - \frac{N_{j-0.5}^{i+1}}{2} C_{j-1}^{i+1} = \\
 & \frac{N_{j+0.5}^i}{2} C_{j+1}^i + \left( 1 - \frac{N_{j+0.5}^i}{2} - \frac{N_{j-0.5}^i}{2} \right) C_j^i + \frac{N_{j-0.5}^i}{2} C_{j-1}^i
 \end{aligned}
 \tag{12}$$

and at the surfaces of the polymer:

$$\begin{aligned}
 & -N_{L-0.5}^{i+1} \cdot C_{L-1}^{i+1} + (1 + N_{L-0.5}^{i+1}) C_L^{i+1} = \\
 & N_{L-0.5}^i \cdot C_{L-1}^i + (1 - N_{L-0.5}^i) C_L^i
 \end{aligned}
 \tag{13}$$

with the dimensionless numbers :

$$N_j^i = \frac{D_j^i \cdot \Delta t}{(\Delta x)^2}
 \tag{14}$$

### Results

The mean result of interest is concerned with the transfer of the contaminant taking place through the thickness of the package during its processing. It is expressed in terms of profiles of concentration developed through the thickness of the tri-layer package and of kinetics of transfer. As the diffusivity is temperature-dependent, it is necessary to get good knowledge of the process of heat transfer. Thus the temperature-time histories are drawn not only during the heating stage in the heated mould but also during the cooling period in

motionless air, as well as the profiles of temperature developed through the thickness of the package.

Two types of tri-layer packages are considered (Table I) with various thicknesses: the one with the same thickness for each layer (0.1 – 0.1 – 0.1cm) ; the other with larger thicknesses for the functional barrier in contact with the food and for the recycled polymer (0.12 – 0.12 – 0.06cm).

The processing of the package is divided into two different stages which are following in succession: the heating stage of the package when the three polymer layers at room temperature are set and pressed into the slabs of the mould heated at constant temperature, followed by the cooling period in motionless air at room temperature.

The polymer selected for the study is the polyethylene terephthalate (PET) whose thermal and diffusional parameters are shown in Table I. Some thermal parameters are found in the literature[20]. A few data can be shown in the literature for the diffusivity only around the room temperature. The diffusivity at high temperature when the polymer can be melted has to be extrapolated, as well as its temperature dependency, by considering that it follows the temperature dependency of the viscosity of the PET[20].

The scheme of the process of heat transfer and mass transfer is shown in Figure 1 for the two packages with different thicknesses for the three layers.

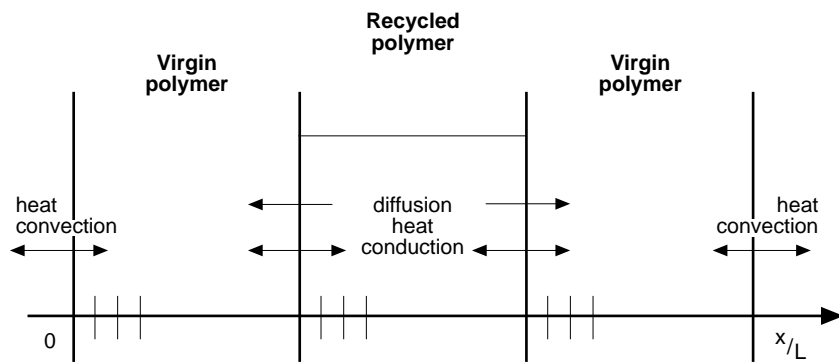
*Heat transfer*

The process of heat transfer is the same for the two packages with different thicknesses for each layer, as the diffusion of contaminant does not intervene in the thermal process. The temperature-time histories are thus drawn in the same Figure 2 for the two packages at various places of interest: on the external surface of the package(1), at relative abscissa x/L of 0.33 and 0.66(3), at the relative abscissa x/L of 0.8(2) and at the relative abscissa x/L of 0.4(4). These positions are those of the interfaces between the polymer layers shown in Figure 1. Of course, these temperature-time histories obtained in the two packages can be drawn in the same Figure 2, as the midplane of each package plays the role of a plane of symmetry.

Thicknesses of the tri-layer package: 0.1/0.1/0.1 cm – 0.12/0.12/0.06 cm

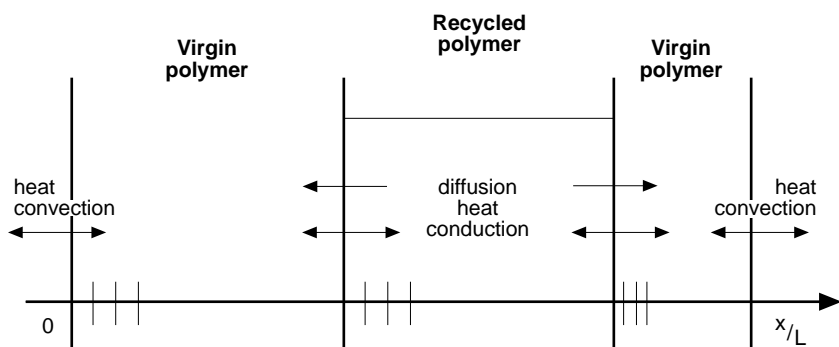
|  |                              |                       |
|--|------------------------------|-----------------------|
| $\alpha = 6.8 \times 10^{-7} \times T + 9.85 \times 10^{-4}$ | (cm <sup>2</sup> /s)         | T : Celsius           |
| $\lambda = 9.6 \times 10^{-8} \times T + 6.1 \times 10^{-4}$ | (cal/cm/s.deg)               | T : Celsius           |
| $h_a^i = 7.1 \times 10^{-4} \times  T_L - T_{sur} ^{0.25}$   | (cal/cm <sup>2</sup> /s.deg) | T : Celsius           |
| $h_m = 0.5$  | (cal/cm <sup>2</sup> /s.deg) | T : Celsius           |
| $D = 28,840 \times \exp\left(-\frac{13,800}{T}\right)$       | (cm <sup>2</sup> /s)         | T : Kelvin            |
| $D_{300} = 10^{-6} - D_{250} = 10^{-7}$                      | (cm <sup>2</sup> /s)         |                       |
| $T_{mould} = 300^\circ\text{C}$                              | $T_{th} = 280^\circ\text{C}$ | $t_h = 23.15\text{s}$ |

**Table I.**  
Parameters of heat  
and mass transfers

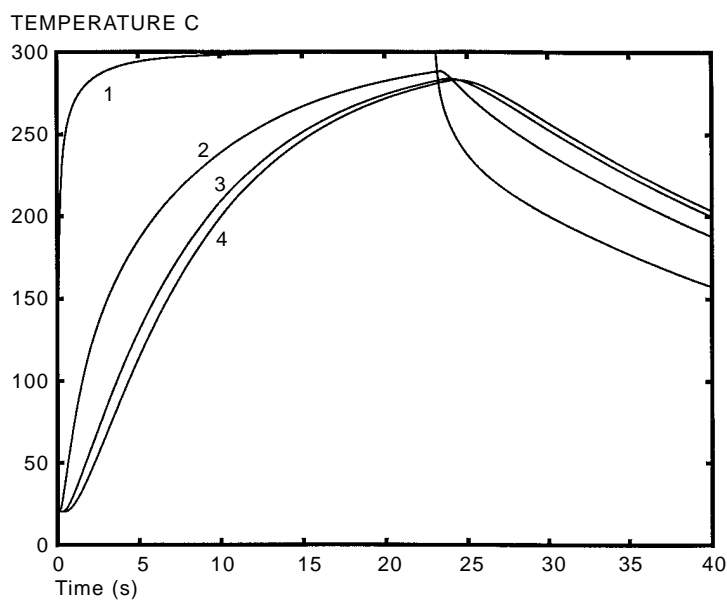


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**Figure 1.** Scheme for the process of heat and mass transfer through the thickness of the three-layer polymer layer package, with the same and different thicknesses

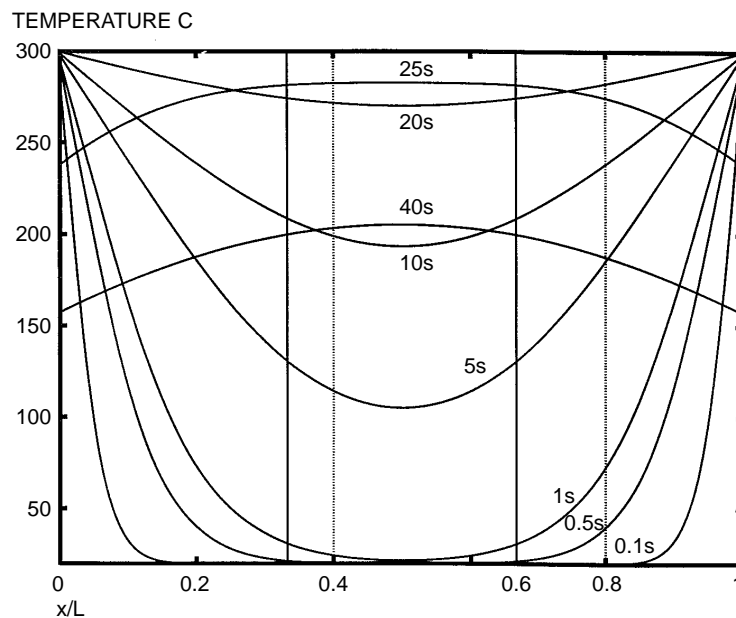


**Figure 2.** Temperature-time histories at various places in the three layer package. 1: surface; 2: at position 0.8 for  $x/L$ ; 3: at position 0.33 and 0.66 for  $x/L$ ; 4: at position 0.4 for  $x/L$

In the same way, the profiles of temperature developed through the thickness of the package during the processing are drawn in Figure 3 for the two different packages.

The following comments can be made from these two Figures 2 and 3 :

- The temperature-time histories drawn in Figure 2 at various places are able to provide a fuller insight into the nature of the process of heat transfer.
- The temperature on each external surface of the package increases very quickly during the heating stage in the mould because of the high coefficient of heat transfer at the slab-package interface. The surface temperature also decreases more quickly than in other places through the package during the cooling period in air.
- Of course the rate of change in temperature is lower during the cooling period in motionless air than in the mould. It results from the fact that the coefficient of heat transfer on the package surface is considerably lower with free convection in motionless air than with good contact in the mould.
- The temperature-time history greatly depends on the position through the package. This fact is clearly shown with the profiles of temperature in Figure 3.
- The maximum of temperature is quite different depending on position in the package, as also shown in Figure 3.



**Figure 3.** Temperature profiles developed through the thickness of the package at various times (the times are noted in S)



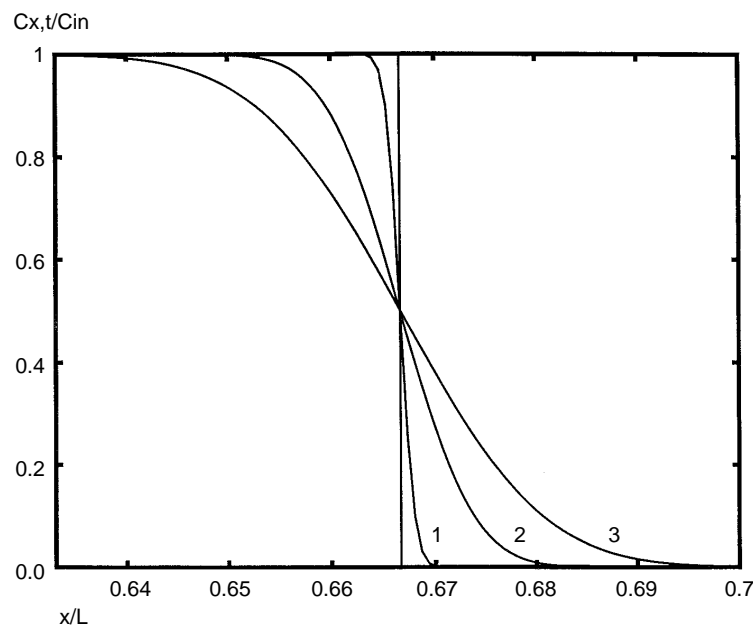
- The profiles of temperature developed through the thickness of the package provide complementary information. The profiles of temperature are symmetrical with the midplane as plane of symmetry.
- Just after the time  $t_h$  at which the package is removed from the mould, the temperature within the package slightly increases, while it decreases quickly on the surface. It results from the time necessary for heat transfer by conduction to take place through the package.
- From the temperature-time histories obtained at each polymer-layer interface, it is difficult to predict the place where the diffusion of contaminant would be larger.

#### Mass transfer

The results obtained for the contaminant transfer through the two layer interfaces are expressed either in terms of profiles of concentration or of kinetics. The profiles of contaminant transferred by diffusion through the thickness of the package at the end of the processing are drawn in Figure 4 for the package with layers of same thicknesses and in Figure 5 for the package with thicknesses 0.12 – 0.12 – 0.06cm. The kinetics of contaminant transfer are shown in Figure 6 at various polymer layer interfaces.

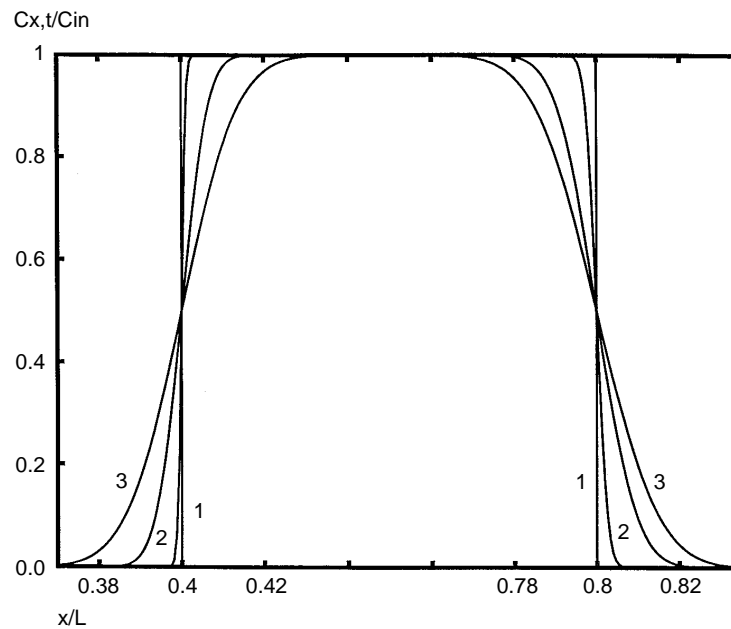
Some results are worth noting :

- Because of the symmetry for heat transfer, a symmetry also exists for mass transfer with the same plane of symmetry at the midplane of the package made of three layers of same thickness.

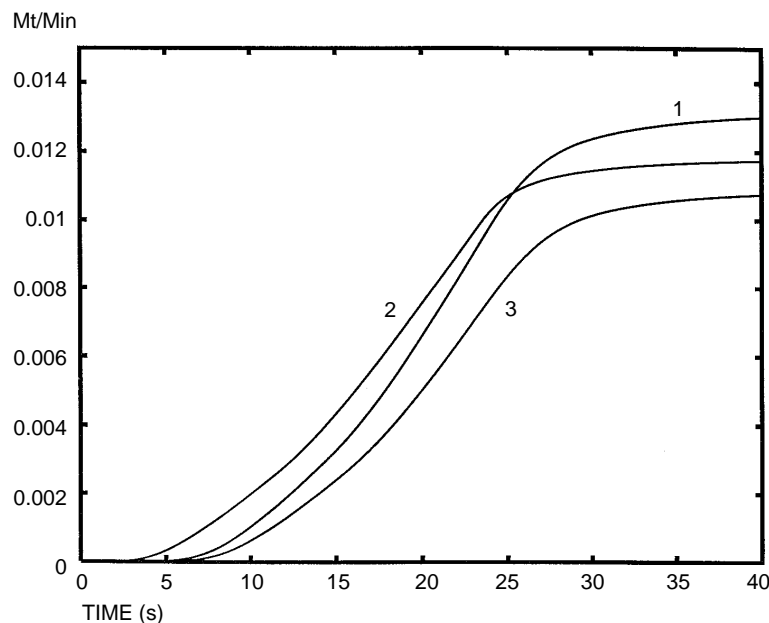


**Figure 4.** Profiles of contaminant developed through the package with three layers of same thickness (0.1 – 0.1 – 0.1cm) at various times: 1: (10s) – 2: (20s) – 3: (40s)

**Figure 5.** Profiles of contaminant developed through the package with three layers of different thicknesses (0.12 – 0.12 – 0.06cm) at position 0.4 for  $x/L$  at various times (10, 20 and 40s) at position 0.8 for  $x/L$  at various times (10, 20 and 40s)



- Resulting from this symmetry, the profiles of concentration in Figure 4 are also symmetrical with the midplane as plane of symmetry. The kinetics of contaminant transfer are also the same in Figure 6 curve 1 at these two positions 0.33 and 0.66 for  $x/L$  when the package is made of three layers of same thickness.
- A difference appears for the contaminant transfer shown either in the profiles of concentration (Figure 5) or in the kinetics (Figure 6) when the package is made of three polymer layers with different thicknesses.
- A typical pattern is followed for the kinetics of contaminant transfer at position 0.8 for  $x/L$  of the package with layers of various thicknesses. In Figure 6 curve 2, the kinetics of transfer is faster at the beginning of the process when the packages is heated in the mould, up to around 23-25s. After this time, the kinetics becomes slower after removal of the package out of the mould. This behaviour can be understood by considering the temperature-time history at this position shown in Figure 2 curve 2 and in Figure 3. At this position the temperature is higher than in the other layer interfaces during the heating period in the mould and it becomes lower during the cooling period in motionless air, being closer to the package surface than the other interfaces.
- At position 0.4 for  $x/L$  in the package with different thicknesses, the kinetics of contaminant is constantly slower than at the other interfaces. This fact is associated with a lower temperature during the heating period in the mould.



**Figure 6.** Kinetics of contaminant transfer at various interfaces. 1: at position 0.33 or 0.66 for  $x/L$  with the package of same thicknesses; 2: at position 0.8 for  $x/L$ ; 3: at position 0.4 for  $x/L$ , with the package of different thicknesses for the layers

- The kinetics of contaminant transfer, expressed by the amount transferred as a fraction of the initial amount located in the recycled polymer layer, are quite different for the various layer interfaces in the two packages. The profiles of concentration developed at the end of the processing are also different. It stands to reason that this fact makes the problem more difficult for calculating the time of food protection when the package is in contact with food.

### Conclusions

The processing for preparing thick food packages made of a recycled polymer layer laid between two virgin polymer layers is rather complex. The processes of heat and contaminant transfers must be considered simultaneously. The process of heat transfer can be divided into two stages: the one when the polymer layers at room temperature are set in the slabs of the heated mould, and the other after removal of the package out of the mould. Various profiles of temperature are thus developed through the thickness of the package during each stage. Following these heating stages, a contaminant transfer is observed at the interfaces limiting the recycled polymer layer. This contaminant transfer, controlled by diffusion with a temperature-dependent diffusivity, is thus closely associated with the temperature-history at each polymer layer interface.

It stands to reason that the effect of the thickness of each polymer layer intervenes in the processes of heat and mass transfer.

As these profiles of concentration of the contaminant developed through the package can be significant for reducing the period of time over which the food is protected from pollution, it becomes necessary to evaluate the diffusivity of

the contaminant at high temperature. Not only should the diffusivity have to be determined at various temperatures close to those used during the package processing, but also the temperature dependency of the diffusivity.

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