

MODELING RELEASE OF CHEMICALS FROM MULTILAYER MATERIALS INTO FOOD

by

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The migration of chemicals from materials into food is predictable by various mathematical models. In this article, a general mathematical model is developed to quantify the release of chemicals through multilayer packaging films based on Fick's diffusion. The model is solved numerically to elucidate the effects of different diffusivity values of different layers, distribution of chemical between two adjacent layers and between material and food, mass transfer at the interface of material and food on the migration process.

Key words: *model, controlled release, migration*

Introduction

Migration of chemicals, such as plasticizers and other trimmer produced during packaging manufacturing, has been a major concern for food packaging industry and has been studied extensively [1-9]. The ability to predict the migration is critical to assess the hazards. However, the current predictive models have many limitations, and the most accurate predictive values were obtained from simple Crank's model [10, 11], which are valid only for uniform packaging materials, and the prediction becomes completely invalid for multi-layer cases, which has a complex boundary and initial conditions, and each layer follows different diffusivity of chemicals [12, 13].

The objective of this paper is to develop a general migration model for multi-layer film consisting of different materials. In this model, one-direction migration, different diffusivities of migrants in different layers, partition coefficient between two layers, partition coefficient between material and food, and mass transfer coefficient between material and food are considered. A series of equations are developed based on Fick's diffusion, and solved numerically by finite difference method [14-16].

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Modeling

Assumptions

The assumptions of this model are:

- all the layers are in perfect contact. Migrant is from the outermost layer to food, fig. 1,
- at the initial stage, the initial concentration of migrant is uniform in the outmost layer,
- the migration is in one direction, *i. e.* from the outermost layer into food, there is no migration from the packaging film into air, and there is a finite coefficient of mass transfer, h_m , from innermost contact layer to food,
- the migration in each layer follows Fick's diffusion, and diffusivities of migrant in each layer are constant,
- the partition coefficients of a migrant are constant at the interface of adjacent packaging layers, and between packaging and food, and
- there is no migration of food into the package.

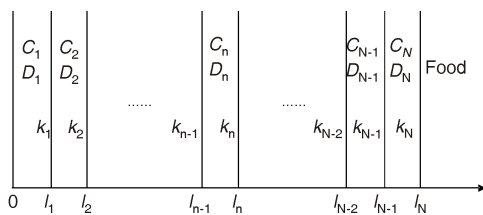


Figure 1. Scheme of model system

The initial conditions are:

$$- t = 0$$

$$C_1 = C_{in} \quad 0 \leq x \leq l_1 \quad (2)$$

$$C_j = 0 \quad l_1 \leq x \leq l_N \quad (3)$$

where C_{in} is the initial concentration of migrant in the outermost layer.

The boundary conditions express the fact that there is no external transfer at $x = 0$; the flux of compound is constant whereas the concentration is not constant at $x = l_j$:

$$- t > 0$$

$$\frac{\partial C_1}{\partial x} = 0, \quad x = 0 \quad (4)$$

$$D_j \frac{\partial C_j}{\partial x} \Big|_{x=l_j} = D_{j-1} \frac{\partial C_{j-1}}{\partial x} \Big|_{x=l_j}, \quad x = l_j, \quad 1 \leq j \leq N-1 \quad (5)$$

$$C_{j-1} = k_j C_j, \quad x = l_j, \quad 1 \leq j \leq N-1 \quad (6)$$

$$D_N \frac{\partial C_N}{\partial x} \Big|_{x=l_M} = h_m \left(C_N - \frac{C_F}{k_N} \right), \quad x = l_N \quad (7)$$

$$C_F = \frac{C_{in} V_m \sum_{j=1}^N M_j}{V_F} \quad (8)$$

Model development

The model is developed based on Fick's diffusion model:

$$\frac{\partial C_j}{\partial t} = D_j \frac{\partial^2 C_j}{\partial x^2}, \quad l_{j-1} \leq x \leq l_j, \quad 1 \leq j \leq N \quad (1)$$

where C_j is the concentration of migrant in layer, j , at position, x , and time, t . D_j is the diffusivity in layer, j .

where k_j and k_N are the constant partition coefficient of compound at the interface between adjacent layers, and between packaging film and food, respectively. The h_m is the constant mass transfer coefficient of migrant at the interface between the inner layer and food. The C_F is the concentration of the migrant in food, and V_F is the volume of food.

The packaging film is divided into a uniform mesh in the direction along film thickness, fig. 2, in which l_N is divided into M parts (h is mesh size, M_j represents j layer material); release time, T , is divided into n parts (time step is τ). The interfaces between adjacent layers are considered to be separated for the convenience of calculation, wherein $1, M_j + j, M_{j-1} + j, M_N + N + 1$ indicate the interface of packaging material and air, j layer material right boundary, j layer material left boundary, and chemical location in food, respectively. Actually, $M_j + j$ and $M_j + j + 1$ are all represented in the size $x = l_j$.

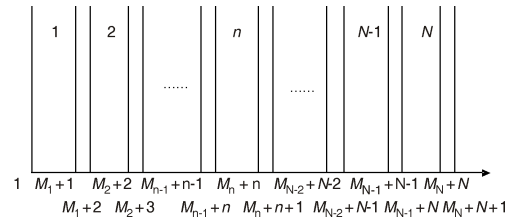


Figure 2. Scheme of model meshing of multilayer packaging material

The following signs are introduced [14, 15]:

$$C_i^{k(1/2)} = \frac{1}{2}(C_i^k + C_{i-1}^k), \quad C_{i(1/2)}^k = \frac{1}{2}(C_i^k + C_{i+1}^k), \quad \sigma_t C_i^{k(1/2)} = \frac{1}{\tau}(C_i^k - C_{i-1}^k),$$

$$\sigma_x C_{i(1/2)}^k = \frac{1}{h}(C_i^k - C_{i+1}^k), \quad \sigma_x^2 C_i^k = \frac{1}{h^2}(\sigma_x C_{i(1/2)}^k - \sigma_x C_{i(1/2)}^k)$$

Equations (1)-(8) can be converted into:

$$\frac{1}{2}\sigma_t C_{ji}^{k(1/2)} - \frac{1}{2}\sigma_t C_{ji}^{k(1/2)} - D_j \sigma_x^2 C_{ji}^{k(1/2)} = 0 \quad (9)$$

$$C_{1i}^0 = C_{in}, \quad 2 \leq i \leq M_1 \quad (10)$$

$$C_{ji}^0 = 0, \quad 2 \leq j \leq N, \quad M_1 \leq i \leq M_N \quad (11)$$

$$\sigma_t C_{1_1}^{k(1/2)} = \frac{2D_1}{h} \sigma_x C_{1_1}^{k(1/2)}, \quad 1 \leq k \leq T_N \quad (12)$$

Left boundary of j layer:

$$\sigma_t C_{jM_{j-1}+j}^{k(1/2)} = \frac{D_j}{h} \sigma_x C_{jM_{j-1}+j}^{k(1/2)} - \frac{D_{j-1}}{h} \sigma_x C_{j-1M_{j-1}+j-1}^{k(1/2)}, \quad 2 \leq j \leq N, \quad 1 \leq k \leq T_N \quad (13)$$

Right boundary of j layer:

$$\sigma_t C_{jM_j-j}^{k(1/2)} = \frac{D_{j+1}}{h} \sigma_x C_{j+1M_{j+1}-j-1}^{k(1/2)} - \frac{D_j}{h} \sigma_x C_{jM_j-j}^{k(1/2)}, \quad 2 \leq j \leq N, \quad 1 \leq k \leq T_N \quad (14)$$

$$C_{j-1M_{j-1}-j-1}^{k(1/2)} = k_j C_{jM_j-j}^{k(1/2)}, \quad 1 \leq j \leq N-1, \quad 1 \leq k \leq T_N \quad (15)$$

$$\sigma_t C_{NM_N-M}^{k(1/2)} = \frac{h_m}{h} C_{NM_N-M}^{k(1/2)} - \frac{C_{FM_N-N-1}^{k(1/2)}}{k_N} - \frac{D_N}{h} \sigma_x C_{NM_N-N-1}^{k(1/2)} = 0, \quad 1 \leq k \leq T_N \quad (16)$$

$$C_{FM_N}^{k(1/2)} = \frac{C_{in} V_1 \frac{1}{2} h^N C_{jM_{j-1}}^{k(1/2)} C_{jM_j}^{k(1/2)} h^N M_j^{j-1} C_i^{k(1/2)}}{V_F} \quad 1 \leq k \leq N \quad (17)$$

The corresponding finite difference scheme is:

$$(1-r_j)C_{ji}^k - (2-2r_j)C_{ji}^{k-1} + (1-r_j)C_{ji}^{k-2} = (1-r_j)C_{ji}^k - (2-2r_j)C_{ji}^{k-1} + (1-r_j)C_{ji}^{k-2}, \quad 1 \leq j \leq N, \quad 1 \leq k \leq T_N \quad (18)$$

Initial conditions:

$$C_{li}^0 = C_{in}, \quad 1 \leq i \leq M_1 - 1 \quad (19)$$

$$C_{ji}^0 = 0, \quad 2 \leq j \leq N, \quad M_1 - 2 \leq i \leq M_N - N \quad (20)$$

Boundary conditions:

$$(1-r_1)C_{11}^k - (1-r_1)C_{12}^k - (1-r_1)C_{11}^{k-1} + (1-r_1)C_{12}^{k-1} = 0, \quad 1 \leq k \leq T_N \quad (21)$$

Left boundary of j layer:

$$\begin{aligned} r_{j-1}C_{j-1M_{j-1}}^k - r_{j-1}C_{j-1M_{j-1}}^{k-1} + (1-r_j)C_{jM_{j-1}}^k - (1-r_j)C_{jM_{j-1}}^{k-1} \\ r_{j-1}C_{j-1M_{j-1}}^{k-1} - r_{j-1}C_{j-1M_{j-1}}^{k-2} + (1-r_j)C_{jM_{j-1}}^{k-1} - (1-r_j)C_{jM_{j-1}}^{k-2} \end{aligned} \quad 2 \leq j \leq N, \quad 1 \leq k \leq T_N \quad (22)$$

Right boundary of j layer:

$$\begin{aligned} (1-r_j)C_{jM_j}^k - (1-r_j)C_{jM_j}^{k-1} - r_{j-1}C_{j-1M_j}^k + r_{j-1}C_{j-1M_j}^{k-1} \\ (1-r_j)C_{jM_j}^{k-1} - (1-r_j)C_{jM_j}^{k-2} - r_{j-1}C_{j-1M_j}^{k-1} + r_{j-1}C_{j-1M_j}^{k-2} \end{aligned} \quad 1 \leq j \leq N-1, \quad 1 \leq k \leq T_N \quad (23)$$

$$C_{j-1M_{j-1}}^{k(1/2)} - k_j C_{jM_j}^{k(1/2)}, \quad 1 \leq j \leq N-1, \quad 1 \leq k \leq T_N \quad (24)$$

$$\begin{aligned} 1 - \frac{1}{2}r_N C_{NM_N}^k - 1 - \frac{1}{2}r_N \frac{h_m \tau}{h} C_{NM_N}^k - \frac{h_m \tau}{hK_N} C_{FM_N}^k \\ 1 - \frac{1}{2}r_N C_{NM_N}^{k-1} - 1 - \frac{1}{2}r_N \frac{h_m \tau}{h} C_{NM_N}^{k-1} - \frac{h_m \tau}{hK_N} C_{FM_N}^{k-1} \end{aligned} \quad 1 \leq k \leq T_N \quad (25)$$

$$\begin{aligned} \frac{1}{2}h^N C_{jM_{j-1}}^k - C_{jM_j}^k - h^N M_j^{j-1} C_i^k - V_F C_{FM_N}^k \\ V_F C_{FM_N}^{k-1} - \frac{1}{2}h^N C_{jM_{j-1}}^{k-1} - C_{jM_j}^{k-1} - h^N M_j^{j-1} C_i^{k-1} - 2C_{in} V_m \end{aligned} \quad 1 \leq k \leq T_N \quad (26)$$

where $r_j = (2D_j\tau)/h^2$.

Conclusion

The paper reports a general mathematical model aiming to predict the migration of chemicals from multilayer packaging material into food. Many important parameters are considered in the model, such as different diffusion coefficient, different partition coefficient, and transmit coefficient at the interface of material and food. Numerical solution is given by iterative computation from finite difference method.

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