

포장된 비타민의 보관수명 예측을 위한 컴퓨터 시뮬레이션

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Computer Simulation to Estimate the Shelf Life of a Packaged Vitamin Tablet

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포장된 복합비타민의 보관수명을 예측하기 위한 수학적모델을 수치해석의 방법 중 finite difference method 을 이용한 컴퓨터 프로그램을 개발하였다. 이 컴퓨터 프로그램에는 포장재료의 수분확산계수와 용해도를 비롯한 식품의 수분확산계수 등 다양한 인자들을 포함하고 있다. 포장재료를 통과하는 수분의 물질전달은 G.A.B water sorption isotherm을 기본으로 했다. 본 연구에서는 비정상상태에서의 물질전달로 기본 수학적 모델링을 구하였다. 본 수학적모델과 프로그램의 결과는 실험치와 비교하지 않았고 대신 특정한 경우를 가상하여 이에 존재하는 analytical solutions를 실제로 구하여 본 수학적모델과 컴퓨터 프로그램의 신뢰도 측정을 하였다.

Keywords: Mathematical model; computer simulation; shelf life; vitamin tablet; moisture transfer.

Introduction

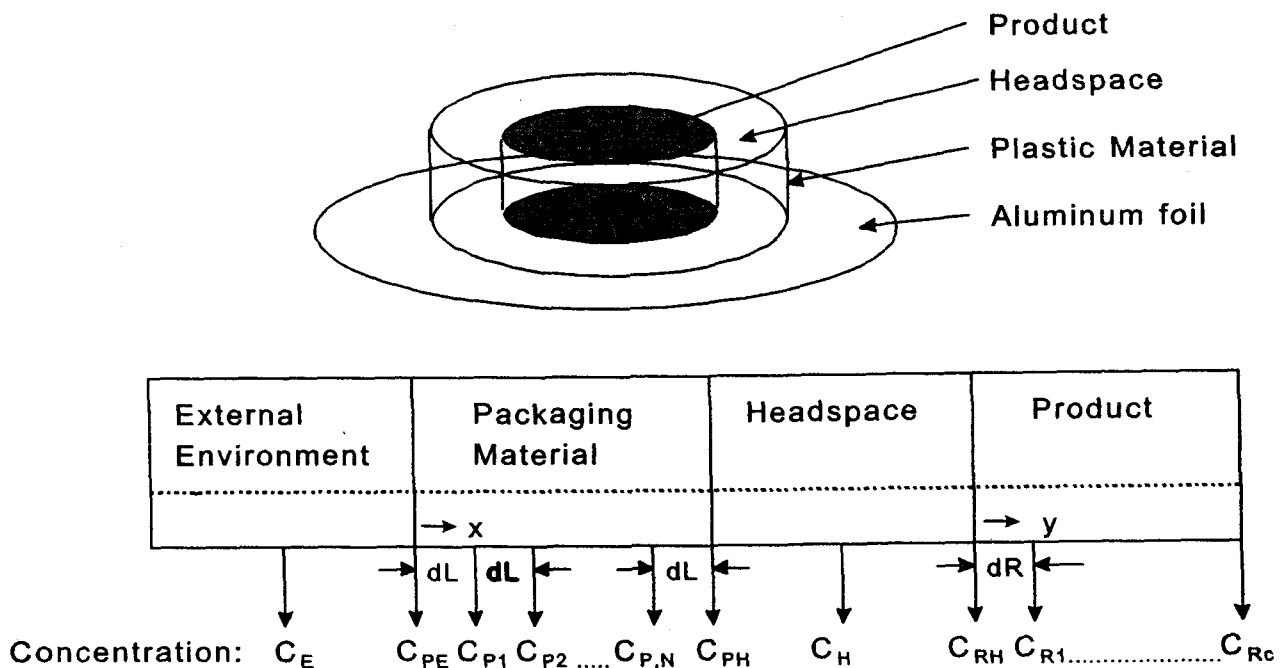
Calculation of the moisture transfer in a packaging system is essential to the shelf-life of moisture sensitive food products packaged in polymeric packaging material. Experimental determination of the shelf life of moisture sensitive food product requires a considerable amount of time and money. Computer programs are needed to develop for estimating the shelf life of packaged products. The availability of many computer models is important not only in reducing cost and time in the estimation of shelf life but also provides a tool to optimize packaging design.

Several predictive models have been prepared in the previous studies. Heiss (1) developed a shelf life predictive model by using concepts of mass transfer. He developed a mathematical model describing the moisture change of a packaged moisture sensitive product for constant temperature and humidity based on the linearity of the moisture absorption. Karel (2) reported a shelf life simulation model based on Heiss' model. Labuza et al. (3) modified Karel's model by lifting the assumption of the linear sorption isotherm models. They combined non-linear sorption isotherm, such as Oswin isotherm, Kuhn isotherm, and Mizarahi isotherm and also cal-

culated the shelf life when chemical reactions with water occurred. Peppas et al (4) developed a model to account for the sensitivity of both packaged dehydrated food and hydrophobic packaging materials to vapor sorption. They started with the general Nernst-Planck's diffusion equation applicable to the transport of penetrants through polymeric films. They conjugated the equation with several non-li

near sorption isotherm which can be applied to food in a various range of water activities, such as the Langmuir, Halsey, B.E.T., Oswin and Freundlich isotherm by using a numerical method. Wang (5) has described a model for predicting the shelf life of a moisture sensitive product stored at a constant temperature and relative humidity condition. Lee(6) upgraded Wang's model by introducing the

Development of the computer program



1. Development of mathematical model

Figure 1. Diagram of a packaged vitamin tablet in a blister package and symbols used for concentrations of water

- C_E The concentration of water vapor outside the package (constant).
- C_{PE} The concentration of absorbed water vapor on the outside surface of the package (Constant)
- $C_{P,1}$ The concentration of water vapor inside of the packaging material at 1 dL from outside layer of packaging material (variable).
- $C_{P,2}$ The concentration of water vapor inside of the packaging material at 2 dL from outside layer of packaging material (variable).
- $C_{P,N}$ The concentration of water vapor inside surface of the packaging material (variable).
- C_{PH} The concentration of diffused water vapor on the inside surface of the package (variable).
- C_H The uniform concentration of water vapor in the headspace (variable).
- C_{RH} The concentration of absorbed water vapor on the surface of the product from headspace(variable).
- $C_{R,1}$ The concentration of water vapor inside of the product at 1 dR from outside layer of product (variable).
- C_{Rc} The concentration of diffused water vapor at the center of the product (variable).

temperature of the package/environment system as a variable. Another modification included the use of the modified B.E.T. sorption isotherm equation to fit the experimental sorption data of the product. In most cases, the models were based on moisture transport through the packaging material at steady state conditions and/or equilibrium moisture content of the product. However there is a need for taking into consideration the unsteady state transport of moisture, the more realistic state especially with the availability of high barrier polymeric structures.

The specific objective of this research was to develop a computer program based on the finite difference method to calculate the shelf life of a moisture sensitive product during storage and validate it by comparing the analytical solutions which can be obtained in two limiting cases.

A mathematical model was developed for calculating the moisture content of a packaged moisture sensitive vitamin tablet based on the unsteady state mass transfer of water through the package and the tablet by applying a G.A.B. water sorption isotherm. The finite difference method was developed to solve the mathematical model. This mathematical model contained a variety of values of the diffusion coefficient and solubility of water in the packaging material, and the diffusion coefficient of water in the tablet.

The mathematical model was developed based on the following assumptions:

- 1) Water was transferred through the polymer packaging material and product only by molecular diffusion.
- 2) The sorption isotherm of product is known, and the sorption of water in the

polymer follows Henry's Law.

- 3) The diffusion coefficients of the polymer and product are known and depend on temperature only.
- 4) The temperature and the relative humidity outside the package are constant.
- 5) Sorption/desorption hysteresis in the product is negligible.
- 6) The water vapor concentration in the headspace surrounding the product is always homogeneous.
- 7) Concentrations of water in the interface between product, headspace, and packaging material are all in thermodynamical equilibrium.
- 8) The product has simple geometry such as a sphere and circular plate. In the latter case, transfer of water occurred only through both circular faces and not through the edge.
- 9) The G.A.B. sorption isotherm curve has linearity from 3% moisture content to 4%.

Water vapor concentrations in the packaging material(CPN,t) at time t.

$$\frac{\partial^2 C}{\partial X^2} = \frac{1}{D_P} \frac{\partial C}{\partial t} \quad (1)$$

Fick's law applied to a thickness dX of packaging material located at a distance X into the material can be written as follows:

where C is the concentration of water (grams/ml of packaging material), and D_P is the diffusion coefficient for water in the packaging material (Fig. 1).

Equation (1) is subject to the following initial condition: at t=0, 0 ≤ x < L, C = C_Pⁱ.

boundary condition: at $t > 0$,

at $x = 0$, $C = C_{PE}$ (constant)

at $x = L$, $C = C_{PH}$

where C_P^i is initial concentration of water in package (g/ml).

Applying the finite difference method to eqn.(1), solution of eqn.(1) is

$$C_{x,t+\Delta t} = Q C_{x-\Delta L,t} + (1-2Q)C_{x,t} + Q C_{x+\Delta L,t} \quad (2)$$

where $Q = D_P \Delta t / (\Delta L)^2$.

Water concentrations at the internal surface of the packaging material (C_{PH}), the headspace (C_H), and the surface of packaged product (C_{RH}) at time $t > 0$

A mass balance of water around the packaging headspace relates the concentrations of diffusing water molecules at the internal surface of the package (PKG) C_{PH} , the headspace C_H , and at the surface of the product C_{RH} at any time $t > 0$. The headspace mass balance is as follows:

$$(-DA \frac{\partial C}{\partial X})_{PKG} - (-DA \frac{\partial C}{\partial y})_{product} = V_H \frac{\partial C_H}{\partial t} \quad (3)$$

where V_H is the volume of the headspace.

Equation (3) is subject to the following initial Condition : at $t = 0$, $C_H = C_{H,t=0}$.

Equation (3) can be cast into a finite difference solution, and the following expression is obtained:

$$C_{H,t+\Delta t} = C_{H,t} + \alpha(C_{P,N-1} - C_{PH})_{PKG} + \beta(C_{R,1} - C_{RH})_{Product} \quad (4)$$

where

$$\alpha = \frac{\Delta t}{V_H} \left(\frac{DA}{\Delta L} \right)_{PKG}, \beta = \frac{\Delta t}{V_H} \left(\frac{DA}{\Delta R} \right)_{Product}$$

The concentration on the internal surface of the packaging material, C_{PH} , is obtained directly from the headspace concentration using Henry's Law.

$$C_{PH} = H_P C_H \quad (5)$$

The product surface concentration, C_{RH} , is obtained by using the G.A.B. sorption isotherm given.

$$A_w = C_H / C_{sat} \quad (6)$$

Since 1 gm of air occupies a volume of

$$V = nRT/p = 1.5829 T \quad (7)$$

where n is $1g/(28.8 g/mol)$, R is $45.59 ml atm/(mole \cdot ^\circ R)$, and p is 1 atm.

The concentration of water in air at saturation (g/ml) is:

$$C_{sat} = AH/1.5829T \quad (8)$$

With given temperature and relative humidity values of the storage conditions, the absolute humidity, AH , obtained from a psychrometric chart at adiabatic saturation temperature is given in grams of moisture per a gram of air.

Initially the headspace concentration, C_H , is calculated using eqn.(4), and C_{sat} is calculated by eqn.(8). After time > 0 , A_w in G.B.A. sorption isotherm is calculated by eqn. (6). Then $A_{w,t+\Delta t}$ can be calculated by G.A.B. sorption isotherm to calculate the moisture content at the surface of product, M . where M is in gm $H_2O/100$ gm dry product, a , b , and c is G.A.B constant.

$$M = \frac{A_{w,t+\Delta t}}{a(A_{w,t+\Delta t})^2 + b(A_{w,t+\Delta t}) + c} \quad (9)$$

Therefore,

$$C_{RH} = M W_s / (100 V_R) \quad (10)$$

where W_s is dry weight of product, V_R is volume of product.

Water concentrations inside the plate shaped product

Fick's law applied to a thickness dy of product located a distance y into the product (Fig. 1) can be written as follows:

Where D_R is the diffusion coefficient for

water in the product.

$$\frac{\partial^2 C}{\partial y^2} = \frac{1}{D_R} \frac{\partial C}{\partial t} \quad (11)$$

Equation (11) is subject to the following conditions:

initial condition : at $t = 0$, $0 \leq r \leq R$, $C = C_{RH,t=0}$

boundary condition : at $t > 0$, $r = 0$, $C = C_{RH}$

Applying the finite difference method to eqn.(11), eqn.(12) is obtained,

$$C_{y,t+\Delta t} = G C_{y-\Delta y,t} + (1-2G)C_{y,t} + G C_{y+\Delta y,t} \quad (12)$$

where $G = D_R \Delta t / (\Delta y)^2$.

For the plate-shape product, concentration of water vapor at the center of the product is the concentration of water vapor at (U/2)th layer, therefore above scheme can be used until the U/2 layer. The concentration at center of the product is obtained from a new boundary condition that the transfer rate through the left layer is zero because $D_R \partial C / \partial r = 0$ at the center.

Therefore,

$$C_{U/2-1} = C_{U/2} (= C_{Rc}) = C_{U/2+1} \quad (13)$$

and $C_{RH} = C_{R,U}$, $C_{R1} = C_{R,U-1}$, $C_{R2} = C_{R,U-2}$

Total water gain for a plate shaped product

Net gain at any time is the sum of average concentrations of each layer times volumes, which can be written as:

$$M_t = (100/W_s) \sum_{i=1}^U M_r \quad (14)$$

2. Development of computer program

The computer programs were written in the FORTRAN language for the different mathematical models developed. The computer flow chart is shown in Figure 2.

The computer program simulated the concentration and amount of water in the vitamin tablet during storage.

Input data for the computer program to simulate the concentration and amount of water in the vitamin tablet during storage are shown in Table 1.

Input data of the computer program

As an application of the computer program, the shelf-life of a multivitamin tablet with a known sorption equilibrium isotherm is calculated. The tablet was packed in a blister package. The computer program analysis includes the study of the following variables on the shelf life of a moisture sensitive product, diffusion coefficient and solubility constant of the water in packaging material, and the diffusion coefficient of water in the product.

1. External environmental conditions surrounding the package

Since the sorption isotherm of the tablet was previously determined at 28°C (6), the following conditions were selected: temperature (T) is 28°C, external environment relative humidity of outside (RH) is 70 %, equivalent to an absolute humidity of outside (AH) is 0.0243 gH₂O/g air.

2. Geometry and dimensions of packaging and product

The surface area of packaging material related to the diffusion of water is 7.54cm², the inner volume of packaging material is 2.2 cm³, and the thickness of the packaging material is taken in 0.005cm. The area of the blister package exposed to the diffusion of wa-

ter through the blister package does not take into consideration the back of the blister generally made of aluminum foil. With respect to the tablet, it was assumed that the diffusion phenomena takes place only through the two circular faces but not through the side area. The surface area (A_R) and volume (V_R) of the circular plate shaped product are 5.67 cm^2 and 1.42 cm^3 .

3. Diffusion coefficient (D_P) and Henry's constant (H_P) of packaging material

In order to minimize computing time, rigid polyvinylchloride (PVC) was selected as a packaging material to run the program. The diffusion coefficient and solubility of water in rigid PVC was obtained from the Polymer Handbook (7). The diffusion coefficient of water (D_P) is $0.024 \times 10^{-6} \text{ cm}^2/\text{sec}$, and the solubility of water (S_P) is $870 \times 10^{-13} \text{ cm}^3 \text{ H}_2\text{O}/\text{cm}^3 \text{ PKG}$. S_P should be converted to

Henry's law constant in $(\text{gH}_2\text{O}/\text{cm}^3 \text{ polymer}) / (\text{gH}_2\text{O}/\text{cm}^3 \text{ Air})$. Henry's constant (H_P), of rigid PVC is $93.28 (\text{gH}_2\text{O}/\text{cm}^3 \text{ PKG}) / (\text{gH}_2\text{O}/\text{cm}^3 \text{ Air})$.

4. G.A.B. constants

G.A.B. constants obtained from the experimental moisture sorption equilibrium data of the multivitamin tablet (M) measured by Kirloskar (8) as a function of relative humidity at 28°C . a is -0.2425096 , b is 0.0079882 , and c is 0.003703545 at 28°C .

5. Initial and critical moisture content

The initial moisture content was taken as a $3 \text{ gH}_2\text{O}/100\text{g}$ dry product, the critical moisture content was considered $4 \text{ gH}_2\text{O}/100\text{g}$ dry product, and the dry mass of the product was taken as 1.7g . These numbers were selected to keep the computer time within a reasonable range.

Table 1. Input parameters of computer program

Componens	Symbol	Values
Outside temperature	T	28°C
Relative humidity	RH	70%
Absolute humidity	AH	$0.0243 \text{ g H}_2\text{O}/\text{g Air}$
Diffusion coefficient of Rigid PVC	D_P	$0.24 \times 10^{-7} \text{ cm}^2/\text{sec}$
Henry's constant	H_P	$93.28 \frac{\text{g H}_2\text{O}/\text{cm}^3 \text{ PKG}}{\text{g H}_2\text{O}/\text{cm}^3 \text{ Air}}$
Thickness of PVC	L	0.005cm
Surface area of PVC	A_P	7.54 cm^2
Volume of blister package headspace	V_P	2.2 cm^3
Number of shells for PVC	N	60
Diffusion coefficient of tablet	D_R	$1 \times 10^{-5} \text{ cm}^2/\text{sec}$
Initial moisture content of tablet	M_i	$\frac{3 \text{ g H}_2\text{O}}{100\text{g dry weight of product}}$
Critical moisture content of tablet	MC	$\frac{4 \text{ g H}_2\text{O}}{100\text{g dry weight of product}}$
Weight of tablet	W	1.7 g
Thickness of tablet	R	0.95 cm
G.A.G. constant	a	-0.2511928
	b	0.3379882
	c	0.003707545
Number of shells for tablet	U	60

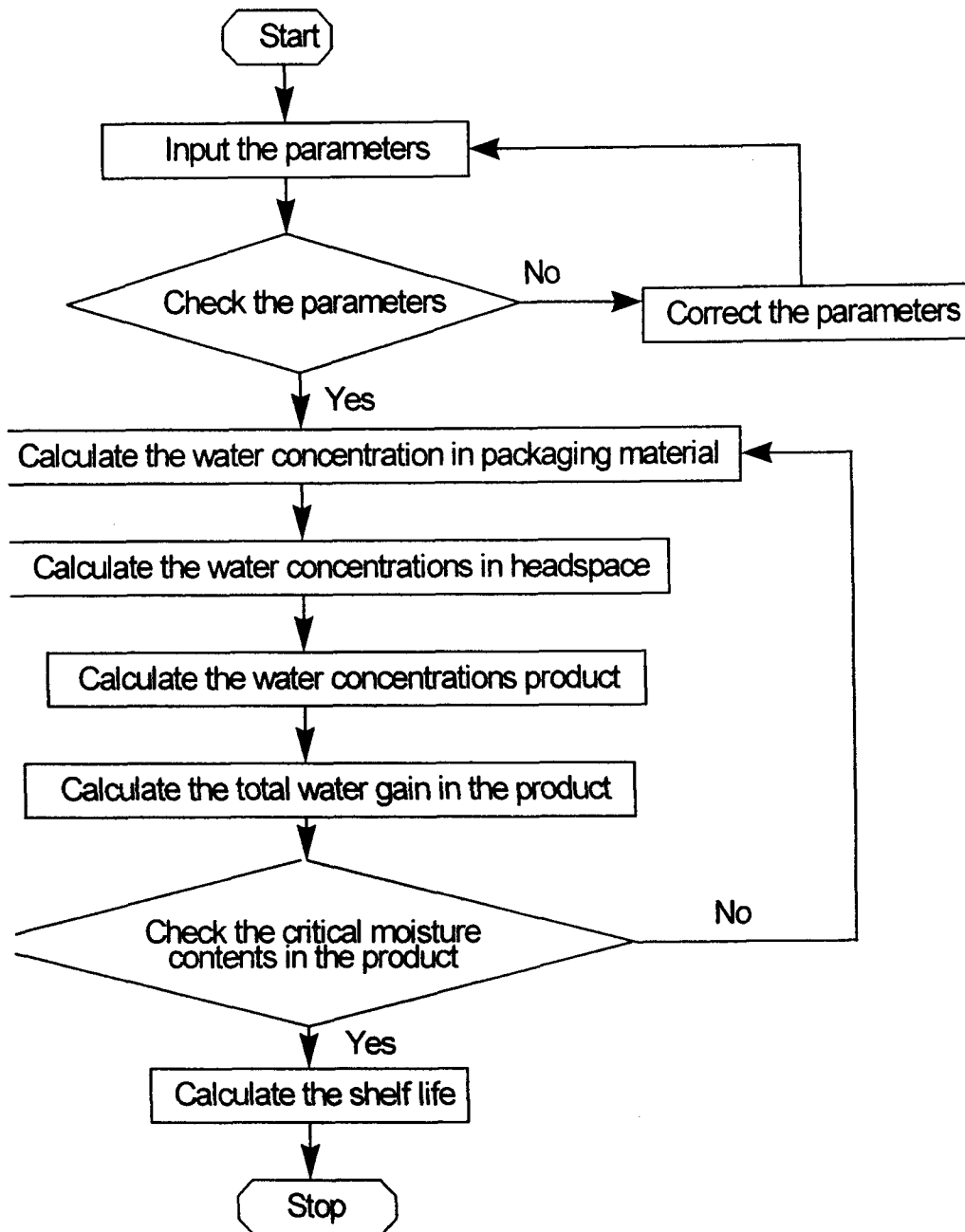


Figure 2. The flow chart of a computer program for obtaining a water concentration profile, and calculating shelf life

Calculation of the analytical solution

Two analytical solutions were developed to compare with the accuracy of the computer program developed only in two limiting cases. One is for the limiting case when the diffusion coefficient of water in the packaging

material is very large, the other for the limiting case when the diffusion coefficient of water in packaged product is very large.

1. Analytical solution of diffusion equation to calculate the concentration of water in packaging material and the

total gain in the circular plate shaped product in a limiting case (when the diffusion coefficient of the packaging material is very large).

The diffusion equation of water in the packaging material was the same as the diffusion equation of water in a circular plate shaped product when they have same initial and boundary conditions, therefore, the solution of equation (1) is the same as that of eqn. (11). Equation (1) is subject to the following

initial condition : at $t = 0$, $C_{x,t} = C_P^i$,
 boundary condition : at $x = 0$, $C_{x,t} = C_{PE}$
 and at $x = L$, $C_{x,t} = C_{PH}$

1). Analytical solution for concentration of water in packaging material and the circular shaped product

The separation variable technique:

The general solution can be obtained by using a separation variable technique,

putting

$$C_{x,t} = X(x)T(t) \quad (15)$$

applying eqn.(15) to eqn.(1) and rearranging,

$$D_P X''(x) T(t) = X(x) T'(t)$$

dividing $X(x)T(t)$, and letting it be equal to $-\lambda^2$ (dummy variable)

$$X''(x)/X(x) = (1/D_P) T'(t)/T(t) = -\lambda^2$$

then,

$$X''(x)/X(x) = -\lambda^2 \quad (16)$$

$$(1/D_P) T'(t)/T(t) = -\lambda^2 \quad (17)$$

so eqn.(16) becomes,

$$X''(x) + \lambda^2 X(x) = 0 \quad (18)$$

the general solution of eqn.(18) is

$$X(x) = C_1 \sin \lambda x + C_2 \cos \lambda x \quad (19)$$

eqn.(17) becomes,

$$T'(t) + \lambda^2 D_P T(t) = 0 \quad (20)$$

the general solution of eqn.(20) is

$$T(t) = C_3 \exp(-\lambda^2 D_P t) \quad (21)$$

applying eqs.(19) and (21) to eqn.(15), and rearranging, $C_{x,t}$ becomes

$$C_{x,t} = (C_4 \sin \lambda x + C_5 \cos \lambda x) \exp(-\lambda^2 D_P t) \quad (22)$$

Calculation of constants in the general solution (eqn.(22)):

A) When $\lambda = 0$,

from eqn.(18) and (20)

$$X(x) = C_6 + C_7 x, \quad T(t) = C_8$$

therefore, the general solution of eqn.(22)

is

$$C_{x,t} = C_9 + C_{10} x \quad (23)$$

applying boundary condition (at $x = 0$, $C_{x,t} = C_{PE}$) to eqn. (23),

$$C_9 = C_{PE}$$

therefore,

$$C_{x,t} = C_{PE} + C_{10} X$$

applying $C_9 = C_{PE}$ and boundary condition (at $x = L$, $C_{x,t} = C_{PH}$) to eqn. (23),

$$C_{PH} = C_{PE} + C_{10} L$$

$$C_{10} = (C_{PH} - C_{PE})/L$$

therefore,

$$C_{x,t} = C_{PE} + (C_{PH} - C_{PE}) (x/L)$$

B) When $\lambda \neq 0$

$$C_{x,t} = \sum_{\lambda=1}^{\infty} (C_4 \sin \lambda x + C_5 \cos \lambda x) \exp(-\lambda^2 D_P t)$$

therefore, in order to satisfy two conditions ($\lambda = 0$, and $\lambda \neq 0$), $C_{x,t}$ becomes

$$C_{x,t} = C_{PE} + (C_{PH} - C_{PE}) \frac{x}{L} + \sum_{\lambda=1}^{\infty} (C_4 \sin \lambda x + C_5 \cos \lambda x) \exp(-\lambda^2 D_P t) \quad (24)$$

In order to get constants C_4 and C_5 in eqn. (24), applying boundary condition (at $x = 0$, $C_{x,t} = C_{PE}$) again to eqn. (24),

$$C_{PE} = C_{PE} + \sum_{\lambda=1}^{\infty} C_5 \exp(-\lambda^2 D_P t) \tag{25}$$

From eqn. (25) it was found out that C₅ must be zero to satisfy the boundary condition.

$$\sum_{\lambda=1}^{\infty} C_4 \sin(\lambda L) \exp(-\lambda^2 D_P t) = 0 \tag{26}$$

In order to get constant C₄ in eqn.(24), applying C₅=0 and boundary condition(at x = L, C_{x,t} = C_{PH}) again to eqn. (24), therefore, C_{x,t} becomes:

$$C_{x,t} = C_{PE} + (C_{PH} - C_{PE}) \frac{x}{L} + \sum_{n=1}^{\infty} (C_n \sin \frac{n\pi x}{L}) \exp(-\frac{n^2 \pi^2 D_P t}{L^2}) \tag{27}$$

$$C_P^i = C_{PE} + (C_{PH} - C_{PE}) \frac{x}{L} + \sum_{n=1}^{\infty} (C_n \sin \frac{n\pi x}{L}) \tag{28}$$

$$\sum_{n=1}^{\infty} \int_0^L (C_n \sin \frac{k\pi x}{L}) (\sin \frac{k\pi x}{L}) dx = \int_0^L [C_P^i - C_{PE} - (C_{PH} - C_{PE}) \frac{x}{L}] \sin(\frac{k\pi x}{L}) dx \tag{29}$$

$$\int_0^L C_n (\sin_2 \frac{n\pi x}{L}) dx = C_n \int_0^L [\frac{1 - \cos(\frac{2n\pi x}{L})}{2}] dx = C_n \frac{L}{2} \tag{30}$$

$$C_n (\frac{L}{2}) = \frac{L}{n\pi} [-(C_P^i - C_{PH}) \cos(n\pi) - \frac{(C_{PH} - C_{PE}) \sin(n\pi)}{n\pi} + (C_P^i - C_{PE})] \tag{31}$$

In order to get C_n in eqn.(27), applying eqn.(27) to initial condition (at t = 0, C_{x,t} = C_Pⁱ)

In order to find C_n in eqn.(28), multiply sin(kπx/L) and integrating from 0 to L. (k=1,2,3,...)

When k ≠ n, integration of right term in eqn.(29) is 0, when k = n, integration of left term in eqn.(29) is:

Rearranging eqn.(29),
rearranging

$$C_n (\frac{L}{2}) = \int_0^L [[C_P^i - C_{PE} - (C_{PE} - C_{PH}) \frac{x}{L}] \sin \frac{n\pi x}{L}] dx$$

Here, sin (nπ) = 0, cos (nπ) = (-1)ⁿ, rearranging.

Therefore, the unknown constant C_n in eqn. (27) is

$$C_n = \frac{2}{n\pi} [-(C_P^i - C_{PH})(-1)^n + (C_P^i - C_{PE})] \tag{32}$$

applying eqn.(32) to eqn.(27), rearranging, and finally the analytical solution to calculate water vapor concentration in the product is obtained.

Therefore,

$$C_{x,t} = C_{PE} + (C_{PH} - C_{PE}) \frac{x}{L} + \frac{2}{\pi} \sum_{n=1}^{\infty} [(C_{PH} - C_P^i)(-1)^n + C_P^i - C_{PE}] \frac{1}{n} \sin(\frac{n\pi x}{L}) \exp(-\frac{n^2 \pi^2 D_P t}{L^2}) \tag{33}$$

2) Analytical solution for total gain of water in a circular-shaped product

$$M(t) = \int_0^L C(x,t) A_P dx \tag{34}$$

Mass at any time, M(t), is

$$M(t) = A_P L [C_{PE} + (C_{PH} - C_{PE}) \frac{x}{2} + \frac{2}{\pi} \sum_{n=1}^{\infty} [(C_{PH} - C_P^i)(-1)^n + C_P^i - C_{PE}] \frac{1}{n} \exp(-\frac{n^2 \pi^2 D_P t}{L^2}) \int_0^L \sin(\frac{n\pi x}{L}) dx] \tag{35}$$

applying C(x,t) in eqn.(33) to eqn.(34)

where

$$\int_0^L (\sin \frac{n\pi x}{L}) dx = [\frac{L}{n\pi} \cos \frac{n\pi x}{L}]_0^L = -\frac{2L}{n\pi}$$

therefore,

$$M(t) = A_P L [C_{PE} + \frac{(C_{PH} - C_{PE})}{2} - \frac{4}{\pi^2} \sum_{n=1}^{\infty} [(C_{PH} - C_P^i)(-1)^n + C_P^i - C_{PE}] \frac{1}{n^2} \exp(-\frac{n^2 \pi^2 D_P t}{L^2})]$$

rearranging,

$$\frac{M(t)}{M_{\infty}} = [1 + \frac{(C_{PH} - 1)}{C_{PE}} - \frac{4}{\pi^2} \sum_{n=1}^{\infty} [\frac{C_{PH} - C_P^i}{C_{PE}} (-1)^n + \frac{C_P^i}{C_{PE}} - 1] \frac{1}{n^2} \exp(-\frac{n^2 \pi^2 D_P t}{L^2})] \tag{36}$$

2. Analytical solution for limiting case (when the diffusion coefficient of the product is very large) for calculating

$$t = \frac{(V_R + ZV_H)L}{H_P A_P D_P Z} \ln \frac{C_H^i - C_E}{C_H(t) - C_E} \quad (47)$$

Results and Discussions

1. The comparison between a finite difference solution and analytical solution in limiting cases

In order to check the accuracy of the finite difference solutions, they were compared to the analytical solutions in some limiting cases. The analytical solutions of the diffusion equations in the packaging material was developed when the penetrant concentrations of both sides of the packaging material are constant. The analytical solutions of diffusion equations of two different shaped products were developed also for limiting cases. When there is no package, the product is exposed to the environment.

2. The comparison between finite difference solution and analytical solution for water diffusion equation in the packaging material

The analytical solution developed for a diffusion equation, eqn.(1), in packaging material in an unsteady state, when surface concentrations of both side are constant. Initial and boundary conditions are as follows,

Initial condition : $t = 0, 0 < x < L, C = f(x)$

Boundary condition : $t > 0, x = 0, C_P = C_{PE}, x = L, C_P = C_{PH}$

where C_{PE} is the water concentration of the outside surface of the plane sheet (at $x = 0$), C_{PH} is the water concentration of the inside surface of the plane sheet (at $x = L$)

The analytical solution (eqn. (33)) and the finite difference solution (eqn.(2)) for the water diffusion equation in packaging material were compared and the results are shown in Figure 3. Two different solutions generated the equal output.

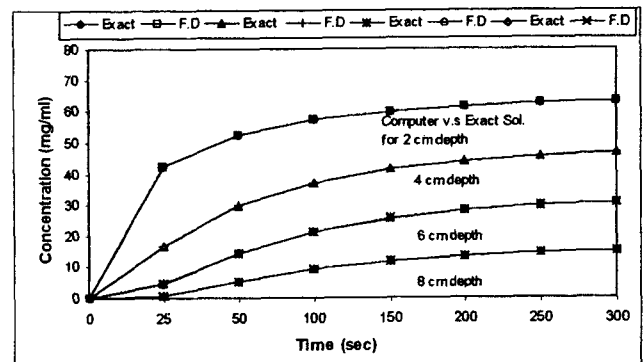


Figure 3. Comparison between an analytical solution and the finite difference solution for calculating water concentration in packaging material

3. The comparison between the finite difference solution and the analytical solution for total gain of water in the plate-shaped product for a limiting case (when the diffusion coefficient of water of the packaging material is very large)

The analytical solution (eqn. (37)) and the finite difference solution (eqn.(14)) for total gain of water in the plate-shaped product were compared and the results are shown in Figure 4. Two different solutions generated the equal output.

4. Analytical solution for the shelf life of a package/product system (vitamin tablet packaged in blister package) in a limiting case when the diffusion coefficient of the product is very large

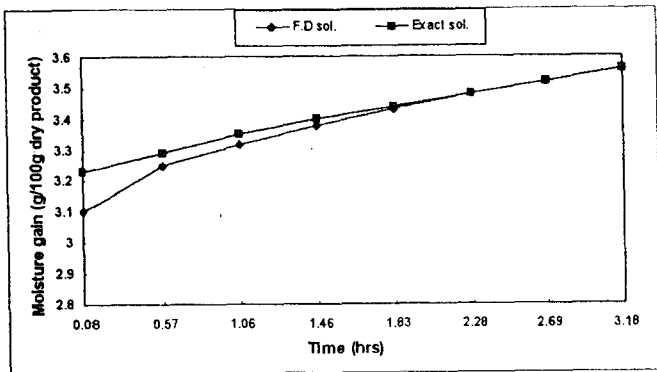


Figure 4. Comparison between an analytical solution and the finite difference solution for calculating total water gain in a plate-shaped product in a limiting case (when the diffusion coefficient of water in packaging material is very large)

In order to check the whole mathematical model based on the finite difference solution and computer program, one analytical solution for a limiting case, that is, when the diffusion coefficient of a product is extremely large, was developed and compared with the finite different solution for packaged plate-shaped products.

The analytical solutions fit very well with the finite difference solutions of the circular plate-shaped product, with three different diffusion coefficients of water in packaging material, in Figure 5. Therefore, in this limiting case, the finite difference solution is very accurate.

In conclusion, the finite difference method applied to the calculation of the shelf life is an effective tool for packaging design in the case of a moisture sensitive product. In limiting cases, the calculated shelf life values agreed well with the shelf life calculated based on the analytical solutions. The percent of error in the case of the circular plate shaped tablet is 0.1%. For further study, the

mathematical model and computer program can be verified by experimentation.

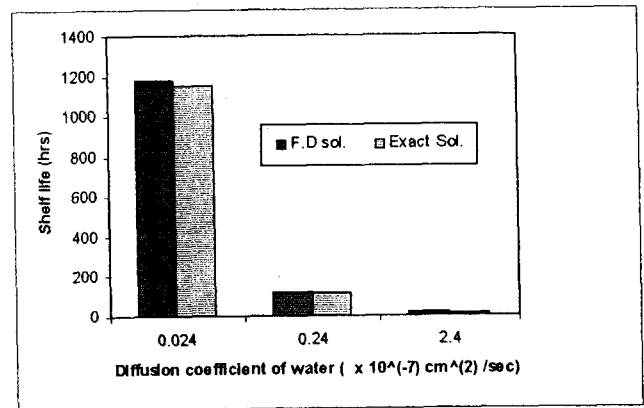


Figure 5. Comparison between an analytical solution and the finite difference solution for calculating shelf life in a packaged plate-shaped product in a blister package for a limiting case (when the diffusion coefficient of water in a product is very large)

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List of symbols

T	Temperature of outside package ($^{\circ}$ R)	H_2O)
RH_E	Relative humidity of outside package (%)	$M(t)$ Total water gain for a plate shaped product (g H_2O)
A_W	Water activity	M_{ri} Moisture content of a layer in the vitamin tablet
AH	Absolute humidity at a given temperature (g H_2O/g air)	M_i Initial moisture content of vitamin tablet (g H_2O / 100g dry Product)
D_P	Water diffusion coefficient of polymer packaging material (cm^2/sec)	M_c Critical moisture content of vitamin tablet (g H_2O / 100g dry Product)
D_R	Water diffusion coefficient of vitamin tablet (cm^2/sec)	W_s Dry weight of vitamin tablet (g)
H_P	Henry's law constant of polymer packaging material (g H_2O/cm^3 PKG)/(g H_2O/cm^3 air)	T_p Thickness of circular plate shape vitamin tablet (cm)
L	Thickness of polymer packaging material (cm)	T Temperature ($^{\circ}$ K)
A_P	Surface area of polymer packaging material (cm^2)	a,b,c G.A.B sorption isotherm constant of vitamin tablet
A_R	Surface area of product (cm^2)	U Number of divided shells of vitamin tablet
V_P	Inner volume of package (cm^3)	t Time
V_R	Inner volume of product (cm^3)	
V_H	Volume of headspace (cm^3)	
C_{sat}	Water concentration in air at saturation (g/ cm^3)	
C_P	Water concentration of polymer packaging material (g/ cm^3)	
C_{Pi}	Initial water concentration of polymer packaging material (g/ cm^3)	
C_{Ri}	Water concentration of packaged product (g/ cm^3)	
C_R	Initial water concentration of product (g/ cm^3)	
$C_R(t)$	Water concentration of packaged product at time (t) (g/ cm^3)	
$C_H(t)$	Water concentration of headspace at time t (g/ cm^3)	
N	Number of divided layers of polymer packaging material thickness	
$CM(t)$	Total water gain for a plate shaped product (g H_2O)	
$M(t)$	Total water gain for a plate shaped product (g	